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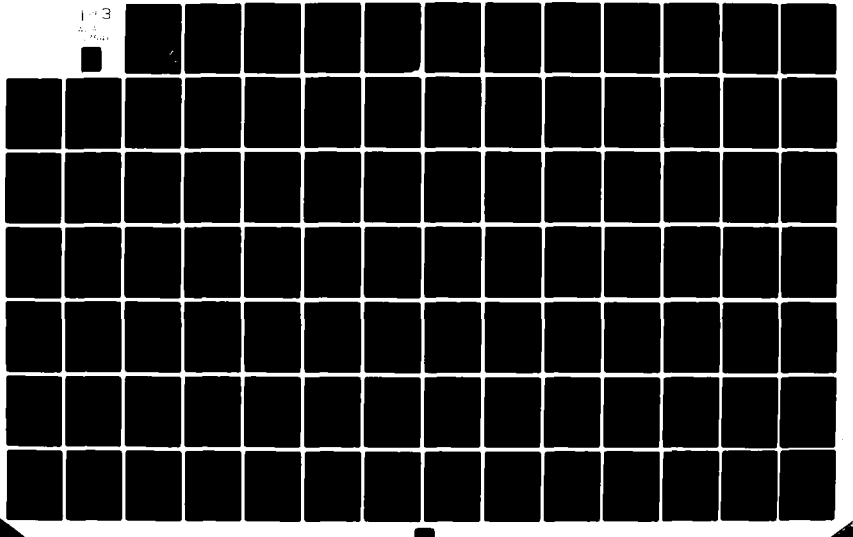

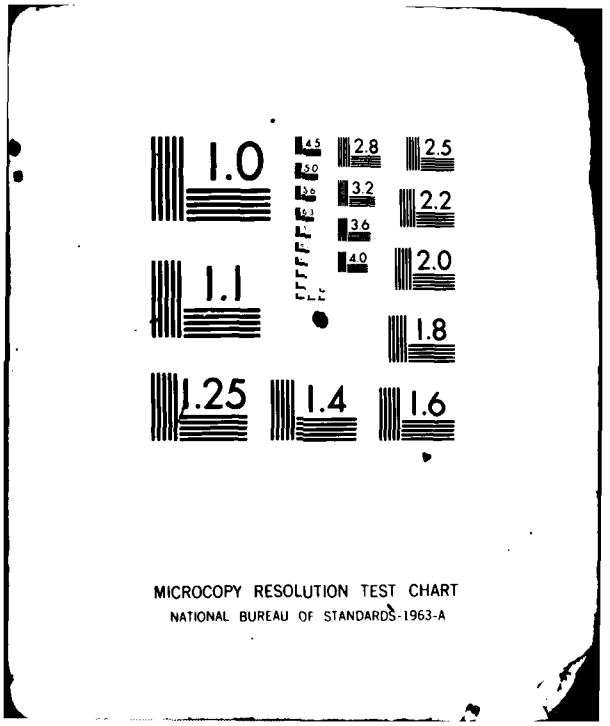
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EVALUATION OF SOLID SORBENTS FOR SAMPLING AND ANALYSIS OF EXPLOSIVES FROM WATER

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July 1982

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Aberdeen Proving Ground, Maryland 21010

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solid sorbents	TNT	PETN
sorbents	2,4-dinitrotoluene	picric acid
resins	2,6-dinitrotoluene	tetracene
explosives	RDX	tetryl
water sampling	nitroglycerine	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report presents the results of a laboratory evaluation of available resins for their efficiency and reliability for sampling low levels of explosives from water for the purpose of quantitative analysis of the explosives. Thirteen different sorbents were evaluated for eight explosives. After the initial screening studies, the most effective resin for each explosive was selected. Each explosive/resin combination was subjected to precision and accuracy testing to determine the detection limit for the explosive in water and the reliability

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of the method. Preservation studies were also performed to determine if the explosives degraded on the resins. The data show solid sorbent sampling to be an easy and reliable method for removal and concentration of explosives from water and easily adaptable to GC or HPLC analysis for the explosives. Detection limits for all the explosives in water were less than 10 µg/L. In general, the Porapak (R or S) resins were superior to the styrene divinylbenzene resins (e.g. XAD-4 or XAD-2) for sampling of explosives in water.

SUMMARY

The objective of this program was to develop and evaluate solid sorbent techniques for sampling and analysis of explosives from water. Initially a literature search was conducted to identify previous resin sampling studies. The data obtained from the literature search were used to select thirteen resins for laboratory evaluation. The thirteen resins were screened and evaluated for their adsorption/desorption of eight explosives (TNT, 2,4-DNT, 2,6-DNT, RDX, tetryl, PETN, nitroglycerine and picric acid). Based upon the screening data, the optimum sorbent for each explosive was selected. The sorbent/explosive combinations were then subjected to four day precision and accuracy testing. The precision and accuracy data show that the solid sorbent sampling and concentration techniques give highly reproducible analyses with detection limits of less than 10 µg/L for all explosives tested. For TNT, 2,6-DNT, RDX and tetryl, the recoveries from the sorbents were essentially quantitative. Recoveries of 2,4-DNT, nitroglycerine, PETN, and picric acid were 85, 68, 52, and 57%, respectively. Once loaded onto the resins, the explosives remain stable for at least three weeks. Desorption after three weeks yield results comparable with same day desorption in all cases except 2,6-DNT and tetryl. In the case of 2,6-DNT, recoveries were only 90% instead of the quantitative recovery found on same day desorption. For tetryl, recoveries only averaged 74%, however, storage time was twice that of the other compounds, i.e. 60 days instead of 22 to 30 days.

One of the surprising results of this study is the relative performance of the resins. In all cases except tetryl, the Porapak resins (R or S) outperformed the styrene divinylbenzene resins (XAD-4 or XAD-2) normally used for sampling of organics from water. The data obtained in this study show that the resins can be reused without loss of adsorption efficiency or carry over. With 20 reuses per sorbent tube, the cost of expendable materials is only $0.32 per sample. The equipment required for sampling hundreds of samples and the preserved samples can be carried in a small suitcase.

The one potential problem with solid sorbent sampling for explosives is the presence of other organics in the water. These organics could lower adsorption efficiencies, promote in situ reactions or interfere with the analysis methods. However, sufficient data are not available to determine if these problems will occur.

In conclusion, the solid sorbents sampling and concentration methods developed under this contract have been shown to be easy, reliable and cost effective. We recommend further evaluation of the methods on actual environmental samples.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

A. Background

Traditionally trace organic pollutants present in surface and ground waters are analyzed by liquid-liquid extraction of the pollutant from the water followed by concentration of the extract before instrumental analysis for quantification. This process necessitates the transport of heavy, bulky containers of water to a laboratory, since one to ten liters of the water samples are generally required for a single analysis. Several problems are often encountered in the collection, transport and analysis of environmental water samples. One of the major problems is the preservation of the sample integrity. Decomposition of the organics and adsorption onto the glass containers often yield analyses that do not give a true picture of the composition of the water. To help eliminate decomposition and minimize adsorption, samples are collected in prewashed amber glass bottles, the bottles packed in a cooler at 4°C and the cooler shipped by air freight to the laboratory. Air freighting large quantities of bulky samples is both expensive and often unreliable. Breakage of the bottles is fairly common and shipments are delayed due to bad weather, etc.

An attractive alternative to the traditional sample collection, shipment and analysis procedures is an "in field" concentration and stabilization technique for organics in environmental waters. Solid sorbent sampling tubes could provide a useful alternative method for sampling and concentrating organics from environmental waters. To be of value in collection of environmental water sampling data, a solid sorbent must meet several criteria:

- the sorbent must efficiently and reliably adsorb low concentrations (< 10 μg/L) of selected organics from large volumes of water
- the organics must be quantitatively desorbed from the sorbent in a form amenable to instrumental analysis procedures
- the organics must not undergo *in situ* reactions or irreversible adsorption on the sorbents
- the organics should be stable on the sorbent for an extended period of time (> 2 weeks)

If sorbent materials which meet the above criteria can be identified, the employment of solid sorbent sampling tubes could cut the expense and improve the reliability of analyses for low levels of organics in environmental waters.

B. Objectives

The objective of this contract was to develop solid sorbent tubes that could be used to reliably concentrate and stabilize low levels of explosives from

ground and surface waters so that the explosives could be later desorbed and quantitated by instrumental analysis. The explosives for which solid sorbent concentrator tubes were to be developed included:

- 2,4,6-trinitrotoluene (TNT)
- 2,4-dinitrotoluene (2,4-DNT)
- 2,6-dinitrotoluene (2,6-DNT)
- hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
- nitroglycerine
- N-methyl-N,2,4,6-tetranitroaniline (tetryl)
- pentaerythrityl tetranitrate (PETN)
- 2,4,6-trinitrophenol (picric acid)
- 4-(1H-tetrazol-5-yl)-3-tetrazene-2-carboxyamidine (tetrazene)
- lead salt of 2,4,6-trinitroresorcinol (lead styphnate)

C. Program Outline

To meet these objectives, the program was divided into two phases. In Phase I, a survey of the literature was performed to identify potential solid sorbent materials for experimental evaluation. Phase II was a laboratory evaluation of the sorbents to identify those sorbents possessing the optimum adsorption/desorption characteristics for each explosive.

The results obtained during this solid sorbents development contract are organized in this report according to the technical program phases as described above. The analytical methodologies used for quantification of the explosives from water and from sorbents are detailed in Appendices B and C along with the QC data on the methods. A brief review of the physical and chemical properties of the explosives studied is presented in Appendix A.

II. SURVEY OF THE LITERATURE AND SORBENT SELECTIONS

A. Survey Methodology

In the literature survey phase, information on solid sorbents and their past uses in environmental monitoring was gathered and evaluated to aid in selection of solid sorbent materials for experimental study. The information was gathered via computerized and manual literature searches and personal communications with manufacturers of various sorbent materials. The computerized data bases searched included Chemical Abstracts, National Technical Information Service (NTIS), Enviroline, Pollution Abstracts, Air Pollution (APTIC), Dissertation Abstracts and the Government Printing Office files (GPO). Manual searches were conducted in Chemical Abstracts from 1950-1970 and through newer volumes of unabstracted journals such as Environmental Science and Technology, Journal of the American Chemical Society, Science, etc.

The data gathered on the various solid sorbents were reviewed and evaluated for the ability of the specific sorbents to meet the following criteria:

- efficiency of adsorption of organics, especially nitroorganics, from water
- capacity of the solid sorbent for nitroorganics
- efficient solvent or thermal desorption of organics, especially nitroorganics, from the sorbent
- low potential for in situ reactions of the sorbate on the solid sorbent
- low potential for intereferences in the adsorption, desorption or analytical procedures

Data on the adsorption of organics from water were abundant in the literature; however, quantitative desorption data were scarce.

The findings of the literature survey and evaluation are presented in the following format in this section. First, the theory of the sorption process is briefly discussed. Then, the properties of the various available sorbents and the results of previous environmental studies using these materials are presented. The selection of sorbents for experimental evaluation and the reasons for their choice conclude this literature survey section.

B. Theory of Sorption Processes

Sorbent materials can be classified into three types based upon the particular sorption process involved. The sorption process can involve:

- the trapping of sorbate molecules in micropores of the appropriate size
- a direct sorbent-sorbate interaction of a hydrophilic or hydrophobic nature
- actual solution of the sorbate in a pseudo "liquid" sorbent
- a combination of these characteristics.

In general, sorbents typically exhibit adsorption by two or more of these processes.

Molecular sieves and activated carbon are examples of sorbents which trap other molecules in micropores. Both molecular sieves and activated carbon have a structure consisting of macropores and micropores, the latter being on the order of molecular dimensions. The application of these materials is dictated by the relative size of the pores to the size of the solute and solvent molecules. Molecular sieves have pore sizes generally less than 1 nm and are thus best suited for trapping small molecules such as water or low molecular weight alcohols from organic solvents. Activated carbon, on the other hand, has pore sizes in the 1-100 nm range and can trap a wide variety of solutes.

The second process involves adsorption via direct sorbent-sorbate interaction of either a hydrophilic dipole-dipole nature or a hydrophobic Van der Waals type. This type of interaction can be illustrated by silica and carbon sorbents. The surface of silica is composed of polar silicon-oxygen or silicon-hydroxyl functional groups which exhibit a strong dipolar attraction with any polar solute. These sorbents are best suited to the removal of polar materials from a non-polar solvent. Carbon and the various polymeric organic sorbents are basically non-polar materials. Non-polar solutes are attracted to these materials by a non-ionic Van der Waals interaction much in the same way that the hydrophobic end of a detergent molecule is attracted to a non-polar oil molecule.

The third process occurs with non-crystalline sorbents. These types of sorbents include semi-liquid organic polymers and bonded or non-bonded liquid phases on a crystalline support base. This process is essentially a partition of solute solubilities between the solvent (water) and the semi-liquid sorbent. It is most effective when the solute is much more soluble in the sorbent than in water. Thus, liquid sorbents cannct be used to remove polar, water soluble organics from water.

For sorption of organics from water, the sorbent should have a relatively large pore size, preferably in the 1 to 10 nm range. The surface properties of the sorbent should be of a hydrophobic nature. Finally, the sorbent should have solubility properties as similar to the solute as possible.

C. Properties and Past Uses of Solid Sorbents in Environmental Analysis

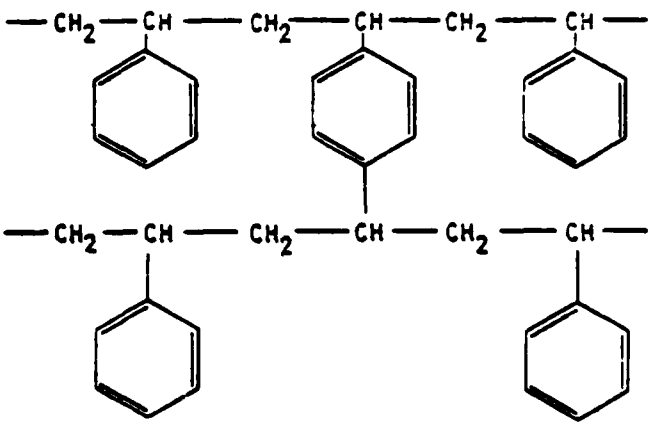
1. Macroreticular Resins

Macroreticular resins are synthetic polymers with high porosity and large surface areas. Typical pore diameters range from 5 to 80 nm and typical surface areas range from 140-800 m^2/g. The resins are generally chemically stable up to 200°C, although some resins can tolerate higher temperatures.

The most common macroreticular resins are polymers of styrene divinylbenzene, acrylic esters, or phenylene oxide. The polymers can have functional groups incorporated chemically into their structures. Common functional groups incorporated in the polymers are acrylonitrile, vinyl pyridine, vinyl pyrrolidone and ethylene glycol dimethacrylate (Analabs, 1980). These functional groups provide chemical selectivity to the polymer which, when combined with size and shape selectivity, yields excellent chromatographic separation of materials.

a. Styrene Divinylbenzene Resins

Styrene divinylbenzene resins are composed of very small gellular microspheres fused into large macrospheres. The space between the agglomerated microspheres is continuously porous. These resins are non-polar and exhibit high sorbent capacity for non-polar sorbates (Pietrzyk and Chu, 1977). The structure of a typical styrene divinylbenzene resin, the Amberlite XAD-2 or XAD-4 resin, is shown below (Kunin, 1976):



Physical properties and typical applications of several commercially available styrene divinylbenzene resins are listed in Table 1. Common styrene divinylbenzene resins are Chromosorb 101 and 102, Porapak P and Amberlite XAD-2 and XAD-4.

The Amberlite XAD resins require preconditioning before they can be used for environmental sampling. For air sampling, Van Rossum and Webb (1978) suggest sequential solvent extraction with acetone, methanol and methylene chloride or chloroform. The treated resins should be stored under a solvent, such as methanol, until needed to prevent sorption of organics while in storage. For water sampling, Rohm and Haas (1978) suggest preconditioning of XAD columns by backwashing with distilled water for approximately ten minutes, followed by downflow of four bed volumes of methanol to remove any traces of preservatives or monomeric components, followed by four bed volumes of distilled water. Since untreated XAD-2 and XAD-4 resins will not be wetted by water, dry sorbent should be wetted with methanol or ethanol before preconditioning.

The styrene divinylbenzene polymers have been used for both air and water sampling of organic pollutants. Of these resins, the Amberlite XAD series resins have been extensively studied for their ability to retain organic pollutants from air and water samples. Available data on air and water sampling with styrene divinylbenzene resins are summarized in Table 2.

In air, humidity appears to have some effect on the capacity (Vg, mL of sorbate per gram of sorbent) of XAD-2 for organics. As shown in Table 3, the sorbent capacity is decreased by as much as 17% at high relative humidity, although the decrease is much smaller for non-polar organics. Sydor and Pietrzyk (1978) report that Amberlite XAD-2 and XAD-4 show a decrease in capacity of 24% and 12%, respectively, in humid atmosphere.

A number of investigators have studied the recovery of organics from water by styrene divinylbenzene resins. The results of several of these studies are summarized below.

Van Rossum and Webb (1978) used the XAD resins to isolate organic pollutants from water. Styrene divinylbenzene resins included in this study were XAD-2 and XAD-4. The resins were used alone and in mixed beds. Recoveries for the various organic species tested using distilled water and tapwater are presented in Tables 4 and 5, respectively. The recoveries of o-nitrotoluene from XAD-2 and XAD-4 were 82 and 83%, respectively. If these data can be extrapolated to the dinitrotoluenes and TNTs, relatively good recovery of these explosives from the XAD-2 and XAD-4 resins can be anticipated. Recoveries of phenol from the XAD-2 and XAD-4 resins were low, 14 and 38%, respectively. Extrapolating these data to picric acid would indicate that these resins would not be suitable as sorbents for picric acid. The reduced recoveries from tapwater are attributed to reaction of the organic compounds with residual chlorine and other materials in the tapwater. Pellizzari and Bunch (1979) also reported that in situ reactions occur on XAD-2 in the presence of olefins and chlorine.

Table 1. Typical Properties of Styrene Divinylbenzene Resins

Porous Polymer	Polarity	Surface Area (m^2/g)	Avg. Pore Diameter nm	Water Affinity	Temp. Limit °C	Application	Reference
Chromosorb 101	Non-polar	30-40	300-400	hydrophobic	275°(325°)*	Fast efficient separation of free fatty acids, glycols, alcohols, alkanes, esters, ketones, aldehydes, hydrocarbons, ethers, etc.	Johns Manville (1980)
Chromosorb 102	Slightly Polar	300-400	8.5	hydrophobic	250°(300°)*	Alcohols, light and permanent gases, oxygenated compounds, adsorbent to trap organics from air or water, etc.	Johns Manville (1980)
Porapak P	Non-polar	110	15	-	250°	Separates a wide variety of carbonyl compounds, glycols and alcohols.	Snyder et al. (1976) Analabs (1980)
Ambersorb XAD-2	Non-polar	300	9	hydrophobic	200°-250°	Concentration of water soluble steroids, surfactants, detergents, aromatic materials, adsorbent to trap organics from air or water.	Snyder et al. (1976) Rohm and Haas (1978)
Ambersorb XAD-4	Non-polar	784	5	hydrophobic	200°-250°	Concentration of organics, aromatics, adsorbent to trap organics from air or water.	Kunin (1976) Snyder et al. (1976)
Porapak Q[a]	Non-polar	840	7.5	-	250°	Particularly effective for hydrocarbons, organic compounds in water, and oxides of nitrogen.	Snyder et al. (1976) Analabs (1980)

*Maximum temperature for short duration

[a]ethyl vinyl benzene-divinyl benzene

- not given

Table 2. Summary of Environmental Adsorption/Desorption Data Available on Styrene Divinylbenzene Resins

Sorbent	Media	Chemicals Sorbed	Capacity g sorbate/g sorbent	% organics of Solution	% Recovery of Organics	Comments	Reference
Porapak P and Q Chromosorb 101 & 102	air	acetonitrile, t-butanol, methyl ethyl ketone, benzene	NG	NG	NG	Porapak Q had highest overall sampling capacity	Butler & Burke (1976)
Amberlite XAD-2 Amberlite XAD-4 Porapak P Porapak Q	air	assorted organics	NG NG NG NG	0.023-4.8 0.40 -8.7 .04 -1.4 .18 -3.5	NG NG NG NG		Sydor & Pietrzyk (1978)
Chromosorb 101 Porapak Q	air	assorted organics	NG NG	NG NG	NG NG	≥ 90% efficient for trapping vapors	Pellizzari et al. (1975a)
Amberlite XAD-2	ethanol-water	assorted nitro- and chlorophenols	NG	NG	> 95%	XAD-2 was used as column chromatography support	Grieser and Pietrzyk (1973)
Amberlite XAD-2	air	n-butyl amine, assorted organics	.000238 g/g sorbent .000107-.000357 g/g sorbent	NG NG	NG NG	some irreversible adsorption occurs for higher boiling adsorbates	Gallant et al. (1978)
Amberlite XAD-2	air	phenol phenol-formaldehyde	NG	NG	93-98%	recovery for phenol in presence of formaldehyde is slightly lower than recovery for phenol alone.	Levin et al. (1977)
Amberlite XAD-2 Amberlite XAD-4	water	assorted organics	NG NG	NG NG	NG NG	Higher adsorption and recoveries were found for SDVB resins than for activated carbon, acrylic esters, carbonaceous resins and anion exchange resins	Glatz et al. (1979)
Amberlite XAD-2 Amberlite XAD-4	water	assorted organics	NG NG	NG NG	44-93% 69-83%	Phenol recovery only, 14% Phenol recovery only, 38%	Van Rossum and Webb (1978)
Amberlite XAD-2 Amberlite XAD-4 Duolite L-863	water	assorted organics	NG NG NG	NG NG NG	NG NG NG	L-863 gives 1.6 times better recoveries than Amberlite XAD-2. Amberlite XAD-4 gives 2.6 times better recoveries than XAD-2.	Chriswell et al (1977)
Amberlite XAD-4	water	TNT and RDX	0.435 g TNT/g sorbent 0.05 g RDX/g sorbent	NG NG	NG NG	Amberlite regenerated but recovery data not given	Stevens et al. (1975)
Amberlite XAD-4	water	TNT, HMX, RDX, tetryl	0.24-0.28 g TNT/g sorbent 0.057 g RDX/g sorbent 0.009 g HMX/g sorbent 0.005 g tetryl/g sorbent	NG	NG	TNT will displace HMX,, RDX, or tetryl	Szachta (1978)
Amberlite XAD-2	water	assorted organics pesticides	NG NG	NG NG	17-97% 24-96%	Although some compounds show low recoveries, most compounds showed recoveries of 80% or better	Harris et al (1980)

NG = not given

Table 3. The Effects of Relative Humidity on XAD-2 Sorption Capacity for Different Sorbates (Piecewicz et al., 1979)

Sorbate	Column Temperature (°C)	% Moisture (vol/vol)	% Relative Humidity	V_g (ml/g)	Relative V_g wet/dry
Pentane	53.1	0	0	1080	-
	53.2	10.9	87	1090	1.00
2-Butanone	53.1	0	0	3430	-
	53.5	9.8	76	2480	0.83
Ethanol	53.1	0	0	280	-
	54.0	10.8	82	244	0.87
Ethyl Bromide	55.0	0	0	640	-
	54.1	11.0	83	615	0.96

Table 4. Percent Recovery of Organics from Distilled Water by Amberlite XAD Resins (Van Rossum and Webb, 1978)

Compound Initial Conc = 50 µg/l.	XAD Resins and Mixtures***									
	7	2/4	8	2/7	2	2/8	2/4/7/8	4	4/8	$CHCl_3$*
Acenaphthene	72	68	20	81	99	85	84	81	81	91
2-Benzothiazole	40	80	53	75	74	73	77	82	82	96
bis(2-chloroisopropyl)ether	**	74	77	76	76	77	71	80	77	92
p-Cresol	33	58	47	50	44	49	60	69	68	50
Dibenzofuran	73	70	95	83	93	86	85	82	84	92
n-Hexadecane	3	**	**	8	3	18	14	**	11	36
1-Methylnaphthalene	64	62	80	75	76	82	80	77	79	86
2-Methylnaphthalene	63	61	77	72	75	80	81	77	77	86
o-Nitrotoluene	53	75	77	79	82	81	81	83	83	91
Naphthalene	64	66	78	77	79	81	82	80	80	87
Phenol	19	30	29	32	14	33	41	38	46	19
α-Terpineol	36	76	62	77	81	75	75	80	80	92
sym-Tetrachloroethane	35	58	59	66	61	68	68	72	72	82
Averages excluding n-Hexadecane	51	65	69	70	71	72	74	75	76	80

* Sample transferred from a beaker to a separatory funnel to simulate adsorption on reservoir wall and then directly extracted with two 50 ml portions.

** Peak unsuitable for accurate quantitation.

*** Mixtures are of equal dry weights of each resin.

Table 5. Percent Recovery of Organics from Tapwater by Amberlite XAD Resins (Van Rossum and Webb, 1978)

Compound	Retained on Reservoir Wall		Recovered from Resin		In Aqueous Effluent from Column	
Initial Conc = 50 µg/L	XAD-2	XAD-4/8	XAD-2	XAD-4/8	XAD-2	XAD-4/8
Acenaphthene	0	2	79	80	0	0
Acenaphthylene	0	0	38 (84)*	42 (83)	0	0
2-Benzothiazole	0	0	69	77	26	30
Camphor	0	0	83	87	5	2
bis(2-chloroethyl)ether	0	0	41 (110)	79 (94)	47	11
bis(2-chloroisopropyl)ether	0	0	85	90	8	0
Di-n-butyl phthalate	4	4	91	92	0	**
Di-(2-ethylhexyl)phthalate	22	19	19	26	43	**
p-Dichlorobenzene	6	6	71	75	0	0
Dimethyl phthalate	0	0	116	113	0	**
Fluoranthene	0	0	85	85	0	**
Hexachlorobenzene	15	11	39	47	28	**
Hexachlorobutadiene	27	30	47	49	0	0
Hexachloroethane	11	12	66	69	0	0
n-Hexadecane	10	19	16	28	42	31
Naphthalene	10	0	84	86	0	0
o-Nitrotoluene	0	0	80	87	0	0
Phenol	0	0	0 (34)	9 (70)	6	0
Pyrene	5	0	64	68	11	
o-Terpineol	0	0	5 (82)	5 (88)	0	0
1,1,3,3-Tetrachloroacetone	0	0	0 (22)	0 (53)	0	0
Tri-n-butylphosphate	4	12	85	72	0	0
2,4,6-Trichlorophenol	0	0	20	25	0	0
n-Tridecane	37	43	4 (5)	9 (6)	18	15

* Values in parentheses are for retests in distilled water (data not the same as presented in Table 4)
** Peaks not suitable for quantitation

Chriswell et al. (1977) studied the recovery of general organic materials sorbed from water using several types of sorbents, including Amberlite XAD-2, XAD-4, XAD-7 and XAD-8, several weak base anion exchange resins and activated carbon. Recoveries were determined relative to the recovery of the XAD-2 resin. Duolite L-863, a styrene divinylbenzene resin manufactured by Diamond Shamrock was 1.6 times more effective than Amberlite XAD-2. Amberlite XAD-4 was 2.6 times as effective as XAD-2. Amberlite XAD-7 and XAD-8 were both 0.6 times as effective as XAD-2. All the other materials tested showed less than 0.2 times the recovery of Amberlite XAD-2.

Harris et al. (1980) also evaluated solid sorbents for water sampling. Among the sorbents considered were Amberlite XAD-2 and XAD-4. Amberlite XAD-2 was used to remove chlorinated pesticides from waste water with recoveries of greater than 89% of the pesticides. The pesticides were desorbed from the resin by elution with diethyl ether. Amberlite XAD-2 was also used to remove polyaromatic hydrocarbons from water with recoveries of 45 to 76%. The XAD-2 resin also removed trihalomethanes from water with greater than 60% recovery. Amberlite XAD-4 was used to remove trihalomethanes and chlorinated pesticides/PCBs with recoveries of greater than 85% and greater than 70%, respectively.

Amberlite XAD-2 or XAD-4 show the greatest affinity for non-polar organics, however, Gallant et al. (1978) have found XAD-2 effective for sorbing alcohols, phenols, alkyl amines and carboxylic acids in addition to less polar organics. Grieser and Pietrzyk (1973) found that nitrophenol and picric acid were retained by XAD-2 to a lesser extent than less polar organics.

Amberlite XAD-4 was used to remove TNT and RDX from munition waste water (Stevens et al., 1975). These investigators found the capacity of Amberlite XAD-4 for TNT to be 0.435 g TNT/g XAD-4. The capacity of XAD-4 for RDX was 0.05 g RDX/g XAD-4. These capacities of XAD-4 were approximately twice the capacity of activated carbon (Filtersorb 300). Approximately 600 bed volumes of "red" water (TNT concentration approximately 100 mg/L) were run through the XAD-4 resin bed before breakthrough occurred. Flow rate was 1 gpm/ft^3. The spent Amberlite XAD-4 could be regenerated with two bed volumes of acetone.

Szachta (1978) summarized the studies on the removal of TNT and RDX, as well as HMX and tetryl, from waste water. Amberlite XAD-4 could remove TNT, HMX, RDX and tetryl from munition waste streams to the level of less than 1 mg/L total nitrobodies. Amberlite XAD-4 has a greater affinity for TNT than for the other nitrobodies. At high concentrations of nitrobodies, competition for sorption sites on XAD-4 occurs, and earlier breakthrough of nitrobodies is found. TNT is adsorbed more rapidly than the other nitrobodies.

While there has been some work published on desorption of organics, none has related directly to the recovery of explosives. Levin et al. (1977) investigated the recovery of phenol from XAD-2. It was found that 97 to 98% of the sorbed phenol could be removed by shaking the resin with diethyl ether. If a phenol-formaldehyde mixture was sorbed by XAD-2, the recovery dropped to 93-

95%. Harris et al. (1980) found that polyaromatic hydrocarbons could be removed from Amberlite XAD-2 with methylene chloride and that diethyl ether could be used to remove pesticides and trichloromethanes from XAD-2 and from XAD-4. Grieser and Pietrzyk (1973) report that nitrophenol and picric acid are released from XAD-2 when the pH of the eluting solvent is increased.

In conclusion, it appears that the styrene divinylbenzene resins can be used to remove many of the explosives of concern from water. Some data are available on XAD-4 and XAD-2 resins for explosives removal from water; however, desorption data are almost non-existant. If extrapolation of the limited o-nitrotoluene data can be made to TNT, the DNTs and tetryl, desorption efficiency is expected to run between 53 and 90% for XAD-2 and XAD-4 resins. No applicable data are available on environmental sampling of explosives with the other styrene divinylbenzene resin, e.g. Chromosorb 101 or 102 or Porapak P.

b. Acrylic Ester Resins

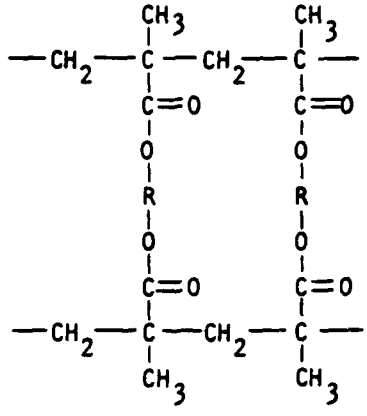
The common acrylic ester resins are Amberlite XAD-7, Amberlite XAD-8, Chromosorb 107, Chromosorb 108, and Porapak T. The structures for Amberlite XAD-7 and XAD-8 are shown in Figure 1. The structures for the other resins are similar. Because of the polarity of the acrylic esters, these resins exhibit a greater affinity for polar sorbates than the styrene divinylbenzene resins (Pietrzyk and Chu, 1977). In addition, the sorbent Porapak T exhibits some water retention (Analabs, 1980). The physical characteristics of these resins are given in Table 6.

The acrylic resins have not been studied to the same extent as the styrene divinylbenzene resins. Chriswell et al. (1977) found that both XAD-7 and XAD-8 showed recoveries of organic contaminants from water of 0.6 times the recoveries found with Amberlite XAD-2. However, the acrylic esters were more efficient than either anion exchange resins or activated carbons. Sydor and Pietrzyk (1978) found that Amberlite XAD-7 had a higher sorbent capacity than XAD-2 for removal of low molecular weight compounds from an air stream. Available sorption data for the acrylic esters are summarized in Table 7. In general, the acrylic ester resins do not appear to be as suitable as the styrene divinylbenzene resins for removal of explosives from water. However, the data are very limited and these resins may be applicable to the more polar explosives such as picric acid.

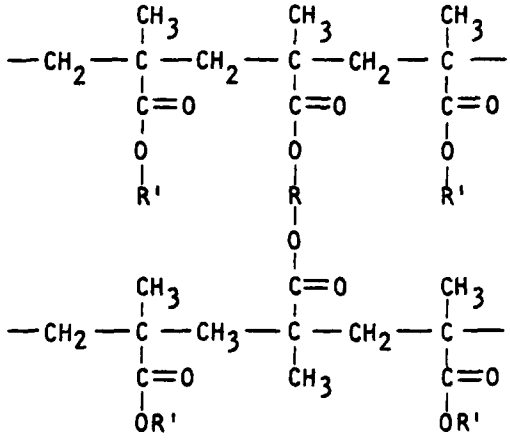
c. Phenylene Oxide Resins

Tenax GC is a porous polymer of 2,6-diphenyl-p-phenylene oxide. Its structure is shown in Figure 2. It was developed as a GC packing material and exhibits the following features (Applied Science Division, undated).

- high maximum operating temperatures (375°C)
- short retention times
- stable baseline after short conditioning time
- effective separation at relatively low tempeatures



Amberlite XAD-7



Amberlite XAD-8

Figure 1. Structures of Amberlite XAD-7 and XAD-8 Resins (Kunin, 1976)

Table 6. Properties of Acrylic Ester Resins

Porous Polymer	Polarity	Surface Area m^2/g	Avg. Pore Diameter (nm)	Water Affinity	Temperature Limit (°C)	Application	Reference
Amberlite XAD-7	Intermediate polarity	450	9	-	200-250	Removal of organics from water	Snyder et al., (1976) Kunin (1976)
Amberlite XAD-8	Intermediate polarity	140	23.5	-	200-250	Removal of organics from water	Snyder et al., (1976) Kunin, (1976)
Chromosorb 107	polar	400-500	8	hydrophilic	225-250	Formaldehyde, sulfur gases, efficient for moderately polar compounds. Adsorbent to trap vinyl acetate from air.	Johns Manville (1980)
Chromosorb 108	polar	100-200	2.5	hydrophobic	225-250	Gases, alcohols, aldehydes, ketones, glycols, etc. Retention characteristics differ from other Century Series supports.	Johns Manville (1980)
Porapak T	polar	450	9.1	hydrophilic	190	Highest polarity and greatest water retention. Determination of formaldehyde in aqueous solutions.	Waters Associates (1979a) Analabs (1980)

Not given

Table 7. Summary of Sorbent Data Available on Acrylic Esters

Porous Polymer	Media	Chemicals	Sorbent capacity g sorbate/g sorbent	% Sorption	% Recovery	Comments	References
Porapak T	air	acetonitrile, benzene, t-BuOH, methyl ethyl ketone	NG	NG	NG	Porapak T shows higher sampling capacity for acetonitrile than styrene divinyl benzene resins	Butler and Burke (1976)
Amberlite XAD-7	air	assorted organics	NG	0.75-7.6	NG	Highest uptake shown for dimethyl formamide	Sydor and Pietrzyk (1978)
Amberlite XAD-7	water	assorted organics	NG	NG	33-72%	Phenol had a recovery of only 19%	VanRossum and Webb (1978)
Amberlite XAD-8			NG	NG	47-95%	Phenol had a recovery of only 29% while acenaphthene recovery was only 20%	
Amberlite XAD-7	water	assorted organics	NG	NG	NG	Recovery was 61% of the XAD-2 recovery	Chriswell et al. (1977)
Amberlite XAD-8			NG	NG	NG	Recovery was 65% of the XAD-2 recovery	

NG = not given

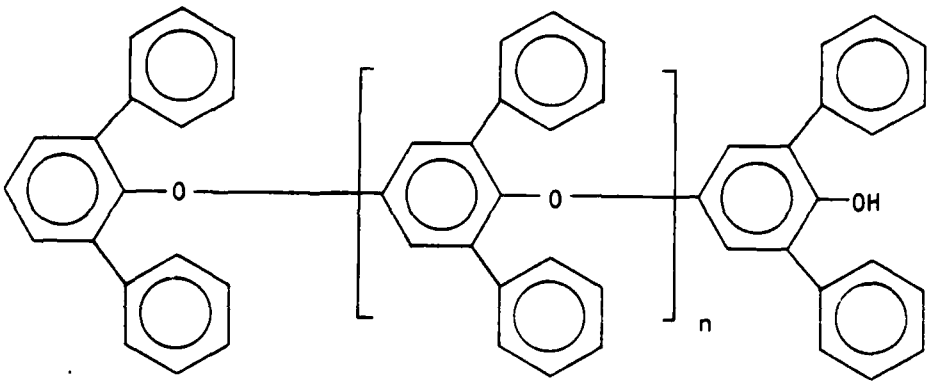


Figure 2. Structure of Tenax GC

Tenax GC is a low capacity sorbent (Sydor and Pietrzyk, 1978). The surface area of the polymer is 19 m^2/g (Butler and Burke, 1976), and the sorbent contains pores varying from 3 nm to 1000 nm (Sakodynskii et al., 1974). The retention volume/unit weight of adsorbent (Vg) is much lower for Tenax than for other sorbents (Butler and Burke, 1976). The relative column capacities (Vg relative packing density) of Tenax GC, Porapaks P, T, R and Q and Chromosorb 101 and 102 are given in Table 8. As can be seen, Tenax consistently has the lowest capacity for these volatile organics (Butler and Burke, 1976). The capacities of the different sorbents for acetonitrile is shown in Figure 3. A summary of sorbent data available for Tenax GC is given in Table 9.

There are conflicting claims concerning Tenax GC's sorbent ability in the presence of water. According to Battelle, Columbus Laboratories (1979), humidity affects the recovery of organics from Tenax. Brown and Purnell (1979) claim that breakthrough on Tenax GC is affected by vapor concentration, but that humidity appears to have no affect on retention volumes. Kuo et al. (1977) used Tenax GC as a sorbent for water soluble organics which were gas-purged from water. When the purging gas contained high water vapor concentrations, displacement of organics from the polymer and more rapid breakthrough were observed. According to the Novotny et al. (1974), water vapor was not retained by Tenax GC but condensation of water on the sorbent decreased the adsorption ability of Tenax GC. Piecewicz et al. (1979) showed that a variation of humidity from 0% to 80% would result in a decrease in retention volume on Tenax GC. The decrease varied from 22 to 43% depending upon the nature of the volatile organic. A comparison of retention volumes at 0 and 80% relative humidity using Tenax GC sorbent is shown in Table 10. In contrast, Barrett (1976) claims 100% recovery of nitroglycerine or ethylene glycol dinitrate independent of humidity. Pellizzari et al. (1976) also claimed that sorbent ability is not affected by humidity levels up to 50%.

There is evidence of Tenax GC decompostion to diphenyl quinone (DFQ) in the presence of nitrous oxide (Battelle, Columbus Laboratories, 1979). The mixture of sulfur dioxide, nitrous oxide and water also react with Tenax GC to give DPQ (Neher and Jones, 1977; Vick et al., 1977). Bunch et al. (1980) report in situ reactions on Tenax GC to form nitrosamines in the presence of NO_x and ozone. Nitrosamines could also be formed by reaction of secondary amines and nitrogen oxide on the Tenax GC surface. Morpholine has been shown to react with as little as 4 ppm NO_x to form 50% nitrosated morpholine (Roundbehler et al., 1980). Other in situ reactions include the formation of dichlorohexane and trichlorohexane in the presence of chlorine gas. Bromoform and dibromocyclohexane are formed on Tenax GC in the presence of bromine gas (Bunch et al., 1980). Thus, precautions must be taken that the organics recovered from Tenax GC are not artifacts of such in situ reactions.

Tenax GC has been shown to be useful for analysis of alcohols, diols, phenols, amines, aldehydes and ketones (Applied Science Division, undated). The resin shows a greater affinity for alkanes, alcohols and amines than for aldehydes, ketones and phenols (Pellizzari et al., 1975a). Barrett (1976) showed that Tenax GC retained both nitroglycerine and ethylene glycol dinitrate with 100% recovery from the sorbent.

Table 8. Relative Capacities of Sorbents in 1/16 Inch OD Columns (Butler and Burke, 1976)

acetonitrile	Tenax << P < 101 ~ 102 < Q ~ R < T
t-butanol	Tenax << 101 << P << T << 102 << R ~ T
methyl ethyl ketone	Tenax < P << 101 ~ 102 ~ T ~ R < O
benzene	Tenax < P ~ 101 ~ T < 102 ~ Q ~ R

The ordering system is based on the following differences (d) in log (V_g^{20} x RPD):

~ d < 10

< .10 < d < .25

<< d > .25

P, T, Q, R = Porapak P, T, Q, R, respectively.

101, 102 = Chromosorb 101, 102, respectively.

T, R, Q, P = Porapak T, R, Q and P, respectively

101, 102 = Chromosorb 101, 102, respectively

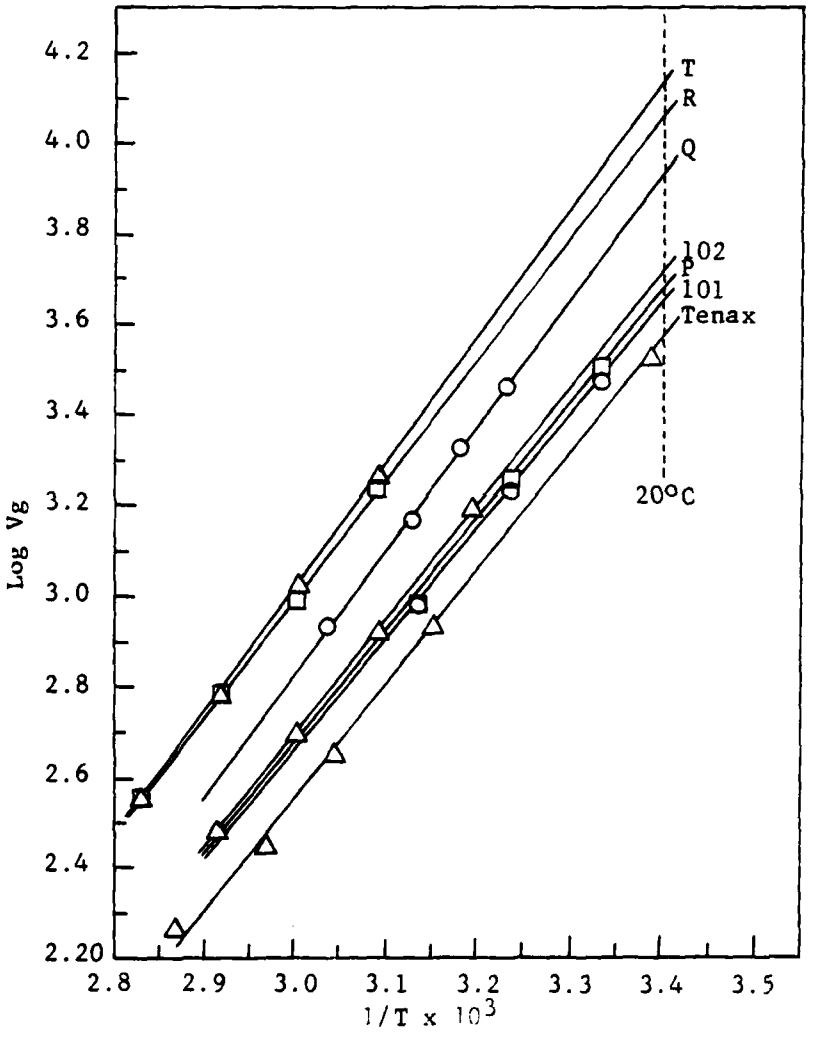


Figure 3. Plots of the Common Logarithm of Specific Retention Volume Versus Reciprocal Absolute Temperature Used to Determine Log V_g Values for Acetonitrile. (Butler and Burke, 1976).

Table 9. Summary of Adsorption Data for Tenax GC

Sampling Media	Chemicals Tested	Sorbent Capacity mg sorbate/g sorbent	% Sorption	% Recovery	Comments	Refeicnces
Air	alkanes	0.08-12.0	NG	NG	Tenax capacity was 50% or less than Amberlite XAD-2 capacity	Adams et al., 1977
Air	acetonitrile, t-BuOH methyl ethyl ketone, benzene	NG	NG	NG	Tenax capacity lower than other porous resins	Butler and Burke, 1976
Air	assorted organics	NG	NG	NG	Adsorption efficiency >75% Desorption efficiency >80%	Kuo et al., 1977
Air	polycyclic organics	NG	NG	30-106%	With Kuderna-Danish concentration of extracting solvents 90-95% recoveries were found	Neher and Jones, 1977
Air	assorted organics	NG	NG	58-95%		Pellizzari et al., 1976
Air	assorted organics	NG	NG	60-100%	For 50 - 300 ng organics on 10.5 x 30 mm Tenax cartridge	Pellizzari et al., 1975b
Air	assorted organics	NG	80-95%	NG	Sampling rate 0.25 L/min.	Pellizzari et al., 1975a
Air	nitrosamines	NG	NG	NG	Tenax has low breakthrough volume for nitrosodimethylamine. Tenax prone to "in situ" formation of artifacts	Roumbehler et al., 1980
Air	assorted organics	NG	0.09-1.62	NG	Uptake ~ 50% of uptake on XAD-2	Sydor and Pietryzk, 1978
Air	assorted organics	NG	>90%	>90%		Versino et al., 1974
Air	nitroglycerin and ethylene glycol dinitrate		104%	100%	Concentration of ethylene glycol dinitrate ranged from 0.27-3.93 mg/m^3	Barrett, 1976

NG Not Given

Table 10. Comparison of Vg's for Sorbates at Two Different Relative Humidities on Tenax GC (Piecewicz et al., 1979)

Sorbate	Column Temp. (°C)	% Relative Humidity	% H_2O	V_g (ml/g)	Relative V_g* $\frac{wet}{dry}$
Pentane	55.5	0	0	536.9	0.57
	54.4	0	0	532.4	
	54.8	83	11	313.7	
	54.4	78	10	295.5	
Ethyl bromide	55.5	0	0	704.0	0.78
	54.4	0	0	688.8	
	54.8	83	11	582.0	
	54.4	78	10	510.5	
2-Butanone	55.2	0	0	3234.9	0.69
	54.4	0	0	3134.2	
	54.8	83	11	2420.5	
	54.4	78	10	1976.9	
Ethanol	55.5	0	0	233.1	0.78
	54.4	0	0	268.3	
	54.3	83	11	205.6	
	54.4	78	10	186.3	

*Relative V_g, $\frac{wet}{dry}$, determined by taking the average wet V_g over the average dry V_g for a given sorbent.

Tenax GC showed an early breakdown when removing nitrosamines from air (Roundbehler, 1980). The Tenax GC air sampler showed 90% retention after 100 L of air had passed through the sampler. But after 190 L of air, the retention has dropped to 7%.

Pellizzari et al. (1976) claim that Tenax GC air sampling cartridges showed good recoveries of sorbates after one week storage with a slight decrease in recovery of sorbates after 2 weeks. These data are presented in Tables 11 and 12.

The high temperature stability of Tenax GC made the polymer a good candidate for solid sorbent hydrocarbon samping tubes to be used for the collection and analysis of organics in air streams (Battelle, Columbus Laboratories, 1979). A sampling tube containing Tenax GC can be fitted to the inlet of a gas chromatograph (GC) and thermally heated. The organics sorbed on the Tenax would elute off the sorbent and be analyzed on-line (Versino et al., 1974). This type of use would eliminate the need to recover organics sorbed on the polymer by solvent extraction. Thermal recovery of volatile organics form Tenax with immediate introduction onto the GC column showed a recovery of 90-100% (Pellizzari et al., 1975b). None of the other common sorbents showed the temperature stability exhibited by Tenax GC.

The major advantage of Tenax GC is its high thermal stability. Sorbates can be removed from Tenax thermally and introduced directly into a GC. In addition, Tenax is particularly suitable for the sorption of high boiling compounds because the combination of high temperature limit and low retention volume would allow rapid desorption of high boiling compounds from Tenax GC. However, data indicate that Tenax GC would not be a good candidate for removal of explosives from water.

d. Other Resins

There are several other solid sorbents resins commercially available. Some of the more popular resins are described in Table 13. The functional groups on these resins make them more polar than the styrene divinylbenzene resins. These resins have so far received only limited study for use as sampling sorbents.

Butler and Burke (1976) compared Porapak R to Porapak P, Q and T, Tenax GC and Chromosorb 101 and 102 for the removal of model compounds from air (see Table 8). Porapak R, a vinyl pyrrolidone resin, exhibited high sampling capacities for the model compounds.

2. Carbonaceous Resins

Rohm and Haas Company has developed a series of sorbents with chemical properties intermediate between activated carbon and polymeric resins. These sorbents, known as Ambersorb XE-340, XE-347 and XE-348, are experimental products not commercially available (Panza, 1981). The affinity for water exhibited by these sorbents varies from the hydrophobic XE-340 to the hydrophilic XE-348. Because of the unique structure found in these sorbents, the Ambersorb

Table 11. Effects of Transportation and Storage on the Percent Recovery of Carcinogenic Vapors from Tenax GC[a] (Pellizzari et al., 1976)

Compound	Weeks Expired				
	Nontransported		Transported		
	0	1	0	1	2
Glycidaldehyde	95	92 ± 4	95	87 ± 4	50 ± 8
β-propiolactone	100	95 ± 4	100	90 ± 5	85 ± 2
Bis-(2-chloroethyl)ether	90	86 ± 6	90	87 ± 5	>95 ± 2
Ethyl methanesulfonate	100	85 ± 5	100	83 ± 6	>95 ± 2
Nitromethane	-*	92 ± 3	-	95 ± 3	85 ± 2
Bis-(chloromethyl)ether	100	65 ± 5	100	58 ± 5	41 ± 4
Butadiene diepoxide	100	76 ± 6	100	75 ± 4	64 ± 5
N-nitrosodiethylamine	100	82 ± 4	100	84 ± 3	62 ± 3
Styrene oxide	100	71 ± 5	100	68 ± 6	70 ± 7

[a]Tenax GC cartridges were loaded with vapors (300 ng/component), shipped by air freight to San Francisco, California and immediately returned. Total transportation time was 6 days.

*Data not given

Table 12. Effect of Storage on the Percent Recovery of Vapors from Tenax GC Cartridges[a] (Pellizzari et al., 1976)

Compound	Weeks Expired		
	0	3	5
1-Nitropropane	95 ± 2	93 ± 3	50 ± 9
Chlorobenzene	95 ± 2	80 ± 4	50 ± 8
Phenyl methyl ether	95 ± 2	95 ± 2	70 ± 8
N-Ethyl aniline	95 ± 2	95 ± 2	70 ± 6
Nitrobenzene	95 ± 2	95 ± 3	50 ± 9
Aniline	95 ± 2	95 ± 2	80 ± 5
4'-Fluoroacetophenone	95 ± 2	80 ± 4	90 ± 4

[a]Tenax GC cartridge samplers were loaded with vapors and immediately shipped air freight to Houston, Texas and returned in two weeks; 0-3 week period includes transport, 3-5 represents additional storage.

Table 13. Physical Characteristics of Selected Macroreticular Resins

Porous Polymer	Type of Polymer	Polarity	Surface Area m^2/g	Avg. Pore Diameter nm	Water Affinity	Max. Temp. °C	Application	Reference
Porapak R	Vinyl pyrrolidone	moderately polar	780	7.6	hydrophilic	250	Moderate polarity. Long retention and good resolution observed for ethers. Separation of esters. Separation of H_2O from Cl_2 and HCl.	Analab, 1980 Snyder et al., 1976
Porapak S	Vinyl pyridine	polar	670	7.6	-*	250	Separation of normal and branched chain alcohols.	Analab, 1980 Snyder et al., 1976
Porapak N	Vinyl pyrrolidone	polar	437	-	hydrophilic	190	Separation of CO_2, NH_3, H_2O, and of acetylene from other C_2 hydrocarbons. High water retention.	Analab, 1980 Snyder et al., 1976
Chromosorb 104	Acrylonitrile divinylbenzene	very polar	100-200	60-80	hydrophobic	250	Nitriles, nitroparaffins, H_2S, xylenols, NH_3, SO_2, CO_2, vinylidene chloride, vinylchloride, traces of water in solvents, etc.	Johns Manville, 1980
Chromosorb 105	polyaromatic	moderately polar	600-700	40-60	hydrophobic	250	Formaldehyde, acetylene from lower HC. Various classes of organic compounds in b.p. range 200°C, adsorbent to trap organics from air and water.	Johns Manville, 1980

- not given

sorbents are characterized by superior performance to conventional sorbents for many applications. The advantages of the Ambersorb sorbents include exceptional physical strength, attrition resistance and increased regeneration flexibility when compared to either activated carbon or to polymeric adsorbents (Rohm and Haas, 1977). The physical characteristics of these sorbents are summarized in Table 14.

Ambersorb XE-340 was designed to adsorb non-polar organics from air or water. It has been proven effective for removing pesticides, such as dieldrin or DDT, halogenated hydrocarbons, and chlorinated ethers from water. Ambersorb XE-347 can be compared to a molecular sieve which separates mixtures by molecular size. The pore structure of Ambersorb SE-347 is an appropriate size and shape for separation of aromatic molecules and unsaturated hydrocarbons. The predominant application of XE-347 has been the removal of organics, such as vinyl chloride, toluene, ethyl acrylate and cumene, from air streams. Ambersorb XE-347 is also suitable for adsorption of organics such as ethanol and acetone from water. Ambersorb XE-348 is a wide spectrum sorbent capable of adsorbing both polar and non-polar organics from either air or water. Ambersorb XE-348 behaves similarly to activated carbon. It can adsorb a wide range of organics and, in addition, is easily regenerated either by solvent extraction or by steam extraction (Rohm and Haas, 1977).

Since these sorbents are still experimental products, limited literature is available on their usage. Harris et al. (1980) used Ambersorb XE-347 in conjunction with Amberlite XAD-2 for the removal of organics from water. A dual bed system was chosen because Ambersorb XE-347 has a greater affinity for polar compounds, such as phenol, than Amberlite resins. Recovery of phenol from water is particularly difficult. Phenol recovery utilizing Amberlite resins XAD-2, XAD-7 and XAD-8 is only 14%, 19% and 29%, respectively (Van Rossum and Webb, 1978). In a dual bed system utilizing Amberlite XAD-2/XAD-8, Van Rossum and Webb (1978) reported recoveries of 48%. Ambersorb XE-347 is capable of recovering 46.8% of the phenol.

These carbonaceous resins have interesting properties which could lead to an effective sorbent system for explosives in water. However, actual data are not available to aid in comparison with other resins. Such data will have to be generated in the laboratory.

3. Other Types of Sorbents

a. C_{18} Reverse Phase Sorbent

Silicone $(C_{18}H_{37}SiO_{3/2})_n$ surface bonded to a silica gel solid support is a common high pressure liquid chromatography packing known as reverse phase C-18 packing. This C-18 packing has been useful for the removal of volatile organics such as car exhaust vapors and chlorinated hydrocarbons from air. Although these organics are effectively adsorbed, there are some indications that the organics desorbed from the C-18 were artifacts of the sorbent (Aue and Teli, 1971). In addition, very volatile organic components in air tend to elute from the C-18 cartridge used in sampling.

Table 14. Typical Physical Properties of Ambersorb™ Resins (Rohm and Haas, 1977)

	Ambersorb XE-340	Ambersorb XE-347	Ambersorb XE-348
Appearance	black, spherical non-dusting	black, spherical non-dusting	black, spherical non-dusting
Total Surface Area (N_2, BET method), m^2/g	400	350	500
Bulk Density, lb/cu.ft.	37	43	37
Bulk Density, g/cm^3	0.60	0.70	0.60
Particle Density, g/cm^3 (Hg displacement)	0.92	1.05	0.91
Skeletal Density, g/cm^3 (He displacement)	1.34	1.85	1.95
Pore Volume, cm^3/g	0.34	0.41	0.58
Particle Size (U.S. Sieve Series)	20-50	20-50	20-50
Crush Strength, Kg/Particle	>3.0	>3.0	1.0
Ash Content, %	<0.5	<0.5	<0.5
Pore Size Distribution			
Diameter Range, nm		Vol. %	
<0.6	0	50	16
0.6- 4	18	0	21
4 -10	13	0	9
10 -30	69	50	51
>30	0	0	3

Waters Associates, Inc. offers a C-18 packed cartridge called a SEP-PAK. These cartridges are designed to perform fast simple clean-up and concentration of organic residues prior to analysis by liquid chromatography (Waters Associates, 1979a). The C_{18} SEP-PAK has been used to concentrate PCBs present at 1 ppb in water, concentrate residues up to one thousand times with 95% recovery, and concentrate large volume samples collected in the field (Waters Associates, 1979b).

Riggin and Howard (1979) used SEP-PAK C-18 cartridges to concentrate benzidine, dichlorobenzidine and diphenylhydrazine present in waste water. The C-18 cartridges allowed for the rapid concentration of the residues. In addition, the recovery of diphenylhydrazine, which is unstable in water, was greatly improved.

Most recently, J.T. Baker Chemical Co. (1981) has commercialized a line of disposable extraction columns similar to the Waters SEP-PAK. The Baker extraction columns are packed with one, three or six ml of C_{18} packing, which makes them more versatile than the Waters SEP-PAK which come in only one size.

Cyano resins are similar to the C_{18} surface-bonded resins except that the $-CH_3$ end group is replaced by -CN. This type of material has intermediate polarity and will sorb strong polar groups better than the C_{18} sorbent. Cyano surface-bonded to silica is available in cartridges from Baker and from Waters.

Since these sampling and clean-up commercial tubes are relatively new on the market, little data are available on environmental sampling and desorption efficiencies. These sorbents have potential for explosives sampling, but additional laboratory data will have to be generated before a good comparison can be made with other sorbent types.

b. Alumina, Silica Gel and Molecular Sieves

Alumina, silica gel and molecular sieves have all been considered as sorbents for air or water sampling, however, they all absorb water more readily than organic materials. In addition, silica gel and alumina are structurally weakened by contact with liquid droplets (Kovach, 1978). Recoveries of 2-aminoethanol adsorbed on silica gel dropped from 100 to 62% when the sorbent tube was stored at ambient temperatures (20°C) for 28 days. A drop of 15% was observed in the first three days of storage (Wood and Nichols, 1978). Since these sorbents show such an affinity for water, their suitability as solvents for water sampling is questionable and they should not be further evaluated in this study.

c. Ion Exchange Resins

Ion exchange resins depend upon electrostatic interactions for the removal or concentration of materials from water. These interactions could severely alter the adsorbed material. For example, Hoffsommer et al. (1977) found that HMX, RDX and other nitrobodies removed from water with the strongly basic anion exchange resins of the Amberlite IRA-400 series reacted on the resin

to form nitrous oxide, ammonia, formaldehyde and nitrite ions. In addition, salts found naturally in ground water could cause premature elution of sorbed material. According to Harris et al. (1980), the anion exchange resins, Amberlite IRA-93 and IRA-904, showed almost instantaneous breakthrough of adsorbed polar organics when the eluting water contained as little as 250 mg/L sodium chloride. This level of salt is not unusual for aqueous effluents, so if ion exchange resins are to be used for adsorbing organics from natural aquifers, the salinity of the aquifer must be considered. The sorbent data available on the use of ion exchange resins for removal of organics from water are summarized in Table 15. Based on the available data, ion exchange resins should not be further evaluated for sorbent for analyzing explosives from water.

d. Polyurethane Foam

Navratil et al. (1977) used open pore polyurethane (OPP) columns to remove polynuclear aromatic hydrocarbons from water. OPP is composed of an agglomeration of microspherical particles in a rigid permeable structure. The OPP columns are prepared in situ by the polymerization of toluene-carbon tetrachloride solutions of isocyanate and polyol. The structures of these materials are shown in Figure 4. Recoveries of the polycyclic aromatic hydrocarbons varied from 56 to 100%. The polycyclic aromatic hydrocarbons were eluated from OPP using methanol. The recovery results are given in Table 16.

Polyurethane foam has also been considered for use as a sorbent for laboratory and river water. The extraction efficiencies of the foam were not as good as either solvent extraction of the water or extraction by XAD resins (Harris et al., 1980).

e. Carbon-Sulfur Compounds

Nonstoichiometric carbon-sulfur compounds (C_xS) have been investigated for the adsorption of phenol from water (Chang and Savage, 1981). Carbon-sulfur compounds behave similarly to activated carbon. Since C-S is not as polar as C-O, it is postulated that aromatic groups would not bind to C_xS as tightly as they do to activated carbon. C_xS was found to have a larger capacity for phenol than Filtersorb 300. In addition, repeated regeneration with 2-propanol solvent extraction recovered 90% of the capacity of the C_xS.

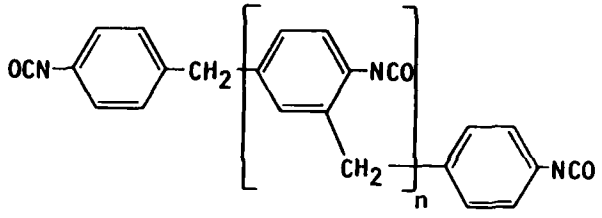
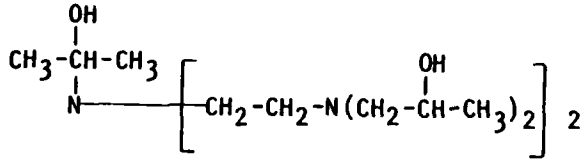
f. Activated Carbon

Activated carbon is an effective sorbent for the removal of most organic compounds from water. Activated carbon is composed of randomly oriented and interfused graphite microcrystals. The interconnected crystals result in a porous, high surface area material. Carbon is activated by first heating to 170°C to remove water followed by heating to 275°C, prolonged heating at 400-600°C and finally by treatment with superheated steam at 750-950°C. The process burns off any hydrocarbon tar coating and enlarges the pore structure of the material. The resulting material has pore sizes varying from less than 2 nm to more than 50 nm. The adsorption efficiency of the carbon is highly dependent on the shape, arrangement and size distribution of the pores (Jonas and Eskow, 1976; Cheremisinoff and Morresi, 1978).

Table 15. Ion Exchange Resins for Adsorption of Organics from Water

Ion Exchange Resin	Type	Materials Sorbed	Results	Reference
Duolite S-37	Weak base anion exchange	assorted organics	17% of the recovery found with Amberlite XAD-2	Chriswell et al., 1977
Duolite A-7	Weak base anion exchange	assorted organics	15% of the recovery found with Amberlite XAD-2	Chriswell et al., 1977
Duolite ES-561	Weak base anion exchange	assorted organics	7% of the recovery found with Amberlite XAD-2	Chriswell et al., 1977
Amberlite A-26	Strong base anion exchange	various phenols	Average recovery of 97.7% of all phenols	Chriswell et al., 1975
Amberlite IRA-93	Weak base anion exchange	phenol	With NaCl content of 250 ppm, breakthrough was instantaneous	Harris et al., 1980
Amberlite IRA-904	Strong base anion exchange	phenol	With NaCl content of 250 ppm, breakthrough was instantaneous	Harris et al., 1980
Amberlite IRA-400	Strong base anion exchange	HMX, RDX explosives	Explosives degraded by ion exchange resin	Hoffsommer et al., 1977
Dowex 1x2	anion exchange	humus materials	60-80% adsorption	Sirotkina et al., 1974
Dowex AV-17	anion exchange	humus materials	60-80% adsorption	Sirotkina et al., 1974
DEAE Cellulose	anion exchange	assorted organics	Adsorption of naphthenic acid, tannin and phenol	Sirotkina et al., 1974
CM Cellulose	cation exchange	assorted organics	No adsorption	Sirotkina et al., 1974

Figure 4. Materials and Reaction for Preparation of Open-Pore Polyurethane of Various Compositions (Navratil et al., 1977)

Trade Name	Structure	Grams of Material per 25 ml Solvent OH/NCO•IQ	QH/NCO•2.2
Mondur MR (Mobay Chemical Co.)		3.16	2.00
LA-475 (Union Carbide Corp.)		2.84	4.00

Reaction: $RNCO + ROH \rightarrow R\text{-}\overset{H}{N}\text{-}\overset{O}{C}\text{-}OR'$

Table 16. Recovery of Polycyclic Aromatic Hydrocarbons with Open-Pore Polyurethane (Navratil et al., 1977

	Flow Rate, L/h	Loaded, µg	Recovery, %
Benzo[a]pyrene	1.8	4	95 ± 6
Biphenyl	0.9-1.5	5-6	98 ± 5
Fluoranthene	0.5-1.0	4-5	77 ± 4
	0.5-1.0	1-2.5	97 ± 3
Naphthalene[a]	0.1	5	56 ± 3
	0.1-1.0	1-2.5	98 ± 10
Phenanthrene	0.8-1.0	5	58 ± 7
	0.8-1.0	1-2.5	92 ± 9
Pyrene	0.6-0.8	1-4	100 ± 2
	1.2-1.7	4-5	89 ± 3
Pyrene (XAD-2)[a]	0.6	4	79 ± 8

[a]Required 10 ml of methanol to elute quantitatively; others needed only 5 ml.

The primary application of activated carbon has been the removal of organic pollutants from water in municipal drinking water or waste water treatment systems. Efficiencies for removal of most organics are high. There are several examples of successful applications of activated carbon in the explosives industry (Cheremisinoff and Morresi, 1978). Szachta (1978) has investigated the relative capacities of activated carbon and XAD-4 in the treatment of "pink water" containing TNT, RDX, HMX and tetryl. Carbon proved to have a higher capacity for all nitrobodies studied except TNT.

Activated carbon has been used extensively to concentrate organics from water for analysis. The carbon adsorption method has several serious limitations, however. High quality activated carbon is not always available, necessitating lengthy preliminary clean-up steps to reduce background levels of organics. Many organics are adsorbed so strongly that desorption efficiencies are low and are not reproducible (Harris et al., 1980; Budde and Eichelberger, 1979).

Chriswell et al. (1977) determined the recovery of organic compounds for a series of sorbents. The recoveries were normalized to the recovery of Amberlite XAD-2. The results are given in Table 17. The activated carbons gave recoveries from 0% to 40% of the recovery found on XAD-2. There are numerous references to the use of carbon adsorption for sampling, a few of which are listed in Table 18. There are also a number of methods which employ carbon sampling tubes (Taylor, 1977).

The difficulty of removing some organics from carbon has been attributed to chemisorption to reactive sites formed by the oxidative activation of the carbon (DeFilippi et al., 1980). It has also been pointed out that improved recoveries result if the carbon is dried well prior to extraction (Van Rossum and Webb, 1978). These data suggest that the hydrophobic extraction solvent is being excluded from the pores by entrapped water. Improved results could be obtained by employing consecutive extractions first with a water soluble solvent, such as acetone or ethanol, before desorbing with a water insoluble solvent, such as chloroform.

The variability of recoveries from different laboratories makes the choice of extraction solvent very difficult. For example, Chriswell et al. (1977) have suggested that diethyl ether is one of the best extraction solvents, while Huffman (1979) has listed the recoveries from diethylether as 0.6%, or almost 100 times less than chloroform. Carbon disulfide is one of the most commonly employed desorption solvents (Taylor, 1977; Graust and Hermann, 1966), but comparisons of it to other organic solvents could not be located. Results obtained in this laboratory (1980) for PCBs demonstrated that chlorobenzene was superior to benzene, acetone or methylene chloride. Presumably the ideal desorption solvent should be as similar to the sorbate as possible.

Table 17. Comparison of Recoveries of Gas Chromatographable Organic Compounds by Various Resins and Carbons (Chriswell et al., 1977)

Sorbent	Type	% Recovery of Gas Chromatographable Organic Compound Relative to XAD-2 Resin				
		Location of Water Source Sampled				
		Ames	Ottumwa	Des Moines	Slater	Average
XAD-2	STDV	100	100	100	100	100
L-863	STDV	75	168	200	188	158
XAD-4	STDV	129	180	577	157	261
XAD-7	ACES	64	21	74	82	61
XAD-8	ACES	83	58	119	3	65
S-761	PHFA	28	10	44	0	21
S-37	AE	16	7	45	0	17
A-7	AE	26	2	32	0	15
ES-561	AE	0	0	26	0	7
Darco	Carbon	3	9	30	0	11
FS-300	Carbon	4	19	31	1	14
WVB	Carbon	17	14	40	0	18
WVG	Carbon	0	20	35	0	14
G-216	Carbon	1	8	26	3	10
G-107	Carbon	19	13	9	3	11
XE-340	Carbon Resin	35	37	24	9	26

STDV - Styrene divinyl benzene; ACES - Acrylic ester; PHFA - phenol formaldehyde; AE - Weak base anion exchange resin

Table 18. Activated Carbon Sampling Studies

Compound(s) Studied	Matrix	Desorption Solvent(s)	% Recovery	Reference
organics	water	freon	0.5	Huffman, 1979
		diethyl ether	0.6	
		methanol	35	
		chloroform	54	
		0.1N HCl	4	
		0.1N NaOH	12	
		steam	28	
Acenaphthene	water	chloroform	0	Van Rossum &
2-Benzothiazole			0	Webb, 1978
bis(2-chloroethyl)ether			85	
hexachlorobutadiene			48	
hexachloroethane			61	
n-hexadecane			14	
phenol			9	
tri-n-butylphosphate			82	
n-tridecane			14	
organics	water	diethyl ether	0-40	Chriswell et al., 1977
methylethylketone	air	carbon disulfide	60-105	Graust and Hermann,
toluene			38-78	1966
trichloroethylene			30-73	
butyl acetate			40-98	
2-methylcyclohexane			59-92	
styrene			22-83	
PCBs (Aroclor 1260)	isopropanol	acetone	0	Unpublished results
		methylene chloride	0	this laboratory,
		benzene	11-16	1980
		chlorobenzene	77-91	

A novel form of solvent extraction has been developed by DeFilippi et al. (1980). The solvent utilized is supercritical CO_2. A large variety of organic compounds exhibit a dramatic increase in solubility near the critical liquid region. Supercritical CO_2 can regenerate carbon upon which organic pesticides had been adsorbed. The resultant carbon has nearly 70% of the capacity of the virgin carbon. These data imply that approximately 30% of the organics are not removed from the carbon. No data were available on recoveries from carbon. Another explanation for the loss in capacity on the carbon might be that interaction of water with active sites on the carbon which could inactivate the sites.

In addition to the problems encountered in removing organics from carbon, it is suspected that in situ chemical changes can occur on carbon. The types of organics desorbed may not represent the types of organics in the water being sampled (Harris et al., 1980).

Conti et al. (1978) mixed modified perlite with activated charcoal for purification of water. The role of the perlite was to increase the removal of non-polar organics from the influent. Modified perlite is a hydrophobic material coated with a layer of silicone oil. The perlite-charcoal mixture removed traces of organics from waste water. The resulting water was of drinking quality.

D. Selection of Sorbents for Laboratory Testing

A wide variety of sorbents have been identified which may have potential for concentrating and stabilizing organics from environmental waters. The properties of the potential sorbents are summarized and compared in Table 19. Under this contract, twelve different sorbents were to be evaluated in the laboratory for their ability to efficiently adsorb explosives from water for chemical analysis. The contract specified four of the sorbents to be tested. These sorbents were:

- Amberlite XAD-2
- Ambersorb XE-340
- Micropak MCH-10
- Surface-bonded C_{18} on Chromosorb G

Surface-bonded C_{18} on Chromosorb G is not a commercially available sorbent (Denboske, 1981); it would have to be custom synthesized at a very high cost. Therefore, Atlantic Research Corporation recommended that this sorbent be dropped from further consideration. This recommendation was approved by the Project Officer. Micropak MCH-10 is a fine mesh surface bonded C_{18} on silica (10 μ particle diameters). Potential pumping problems with this fine sorbent lead to its replacement with the Baker surface-bonded C_{18} on silica cartridges.

Table 19. Summary of Candidate Sorbents for Laboratory Testing

Sorbent	Manufacturer	Specific Surface Area, m^2/g	Average Pore Diameter, nm
A. Styrene Divinylbenzene			
1. Amberlite XAD-2	Rohm & Haas	300	9
2. Amberlite XAD-4	Rohm & Haas	784	5
3. Chromosorb 101	Johns Manville	30-40	300-400
4. Chromosorb 102	Johns Manville	300-400	8.5
5. Porapak P	Waters Associates	110	15
6. Porapak Q (ethylvinyl benzene)	Waters Associates	840	7.5
7. Chromosorb 106 (cross-linked polystyrene)	Johns Manville	-	-
B. Acrylic Esters			
1. Amberlite XAD-7	Rohm & Haas	450	9
2. Amberlite XAD-8	Rohm & Haas	140	23.5
3. Chromosorb 107	Johns Manville	400-500	8
4. Chromosorb 108	Johns Manville	100-200	2.5
5. Porapak T (ethyleneglycodimethyl-acrylate)	Waters Associates	450	9.1
C. Acrylonitrile Divinylbenzene			
1. Chromosorb 104	Johns Manville	100-200	60-80
D. Vinyl Pyrrolidones			
1. Porapak R	Waters Associates	780	7.6
2. Porapak N	Waters Associates	437	-

Table 19. (continued)

Sorbent	Manufacturer	Specific Surface Area m^2/g	Average Pore Diameter, nm
E. Vinyl Pyrridine			
1. Porapak S	Waters Associates	670	7.6
F. Carbonaceous			
1. Ambersorb XE-340	Rohm & Haas	400	10
2. Ambersorb XE-347	Rohm & Haas	350	10
3. Ambersorb XE-348	Rohm & Haas	500	10
G. Activated Carnon			
1. APC 12x46	Calgon	-	-
2. Filtersorb 300	Calgon	-	-
3. Darco 5-51	Darco	-	-
4. C-S Surface Carbon	Exxon Research	-	-
H. C-18			
1. C-18 on Silica	(e.g. Micropak MCH-10) Varian	-	-
2. C-18 on Chromosorb G	Not Available	-	-
I. Miscellaneous			
1. Chromosorb ' S (polyaromatic)	Johns Manville	600-700	40-60
2. Tenax GC	Enka NV	19	72.0
3. Cyano on Silica	Baker	-	-

- Not Given

Most of the studies concerning the use of solid sorbents for water sampling examined styrene divinylbenzene resins such as Amberlite XAD-2 and XAD-4. Both these resins are potentially good sorbents for the nitrobodies of interest to USATHAMA. Other styrene divinylbenzene resins are Chromosorb 102, which is chemically equivalent to XAD-2, Chromosorb 101 and Porapak P. Porapak P has a larger pore size than Amberlite XAD-2 (9 nm) or XAD-4 (15 nm), but its surface area is much lower (110 m^2/g). Since sorbent capacity is related to surface area, Porapak P will not have the capacity of the XAD resins. Chromosorb 101 has a very low surface area (30-40 m^2/g) with a very large pore size (300-400 nm) (Snyder et al., 1976). Since the mechanism for sorbent activity for styrene dinvinylbenzene resins has been postulated to involve van der Waal interactions and the surface area is so low, Chromosorb 101 will have very low capacity and may have only limited applicability to water sampling. Therefore, of the styrene divinylbenzene resins, XAD-4 was recommended for study in addition to the required XAD-2. This recommendation was based on the many examples of superior performance of XAD-4 over that of XAD-2 found in the literature.

Amberlite XAD-7 and XAD-8, Chromosorb 107 and 108, and Porapak T are acrylate esters. The acrylate esters are expected to show higher capacity for polar sorbates than the styrene divinylbenzene resins (Pietrzyk and Chu, 1977). Although the available literature data indicated that the acrylic resins did not show as good a recovery of organics from water as did XAD-2, we did not believe the evidence was sufficient to eliminate the acrylic resins from further study. Therefore, XAD-7 and XAD-8 were included in the laboratory study.

Data on sampling of organics from water was sparce for the vinyl pyrrolidone, vinyl pyrridine and acrylonitrile divinylbenzene resins. This lack of data did not appear to justify eliminating these sorbents from the study. Thus, Chromosorb 104, Porapak R and Porapak S were evaluated in the laboratory.

Tenax GC, a phenylene oxide sorbent, has received much attention for air sampling of organics. It is a low capacity resin (Butler and Burke, 1976) which could exhibit decreased capacity in aqueous media (Piecewicz et al., 1979). In addition, in situ reactions are known to occur on Tenax GC (Neher and Jones, 1977; Bunch et al., 1980; and Roundbehler et al., 1980). Tenax GC was not used for water sampling in any of the literature obtained. The evidence of low capacity of Tenax GC in the presence of water was sufficient to eliminate this sorbent from further consideration.

Carbonaceous resins appear very promising for water sampling. The Ambersorbs have sorbent abilities comparable to activated carbons, but the sorbates are more easily desorbed from the Ambersorb surface. Ambersorb XE-340, XE-347, and XE-348 differ widely in their sorbent properties and were all included in the laboratory studies.

Activated carbon is an excellent sorbent which adsorbs a wide range of organic compounds from water. One of its major advantages is its low cost compared to other sorbents. Disadvantages are that desorption of adsorbed materials from carbon is often difficult and that in situ reactions of sorbates

are suspected. Since activated carbon is known to remove many of the explosives of interest from water, it was included in the laboratory study as a back-up sorbent in case none of the other sorbents proved to be satisfactory.

In summary, the sorbents selected for further study in the laboratory to determine their absorption/desorption efficiency for explosives in water were:

Amberlite XAD-2
Amberlite XAD-4
Amberlite XAD-7
Amberlite XAD-8
Ambersorb XE-340
Ambersorb XE-347
Ambersorb XE-348
Porapak R
Porapak S
Chromosorb 104
Surface-bonded C_{18} on silica
Filtersorb 300

Baker cyano adsorption columns were also included in the laboratory evaluation due simply to their commercial availability.

III. LABORATORY EVALUATION OF SORBENTS

A. Adsorption/Desorption Apparatus Development

1. Adsorption Apparatus

Prior to screening studies, a number of adsorption systems were evaluated. The most important component of the system is the sorbent tube itself. Only two commercially available sorbent tubes were identified, the Waters "Sep-Pak" and a similar system offered by Baker. The Sep-Pak cartridges were judged inadequate for volumes of one liter due to their relatively small size. The Baker cartridges, on the other hand, are available in a variety of sizes, the larger of which could be capable of handling the one liter volumes necessary for collection and analysis of μg/L levels of explosives in water. The Baker "3 mL" cartridges are one cm O.D. plastic syringe barrels packed with approximately one cm of sorbent. The sorbents presently available are a reverse phase C-18 on silica packing and a cyano packing.

As it was necessary to evaluate a wider range of sorbents than those commercially available from Baker or Waters, it was considered essential to develop a sorbent tube which could be conveniently packed with the desired sorbent. Materials considered satisfactory for construction of the tubes were polyethylene, teflon, glass or stainless steel.

One design which was evaluated was a tube fabricated from a section of 5/8 inch O.D., 3/10 inch I.D. heavy wall teflon tubing. Initially, threaded teflon end caps which would accept teflon swagelok unions for connection of the sorbent tube to 1/4 inch O.D. flexible teflon tubing were used. This design was abandoned as being too complicated and was replaced by a system employing stainless steel reducing unions for connection to the 1/4 inch teflon tubing. Although this system was relatively convenient to use, it was judged unacceptable due to high construction costs.

The sorbent tubes ultimately selected were made from 5 mL disposable glass pipets. Disposable glass 5 mL graduated pipets were chosen because: 1) they are relatively inexpensive, and readily available, 2) they can be rapidly filled with a reproducible volume of sorbent, and 3) they have a high length to width ratio which is desirable to prevent leakage (flow of contaminated water past the sorbent without intimate contact with the sorbent) especially at the high flow rates necessary to accommodate convenient collection of one liter of solution in a reasonable length of time. The pipets were packed to the lowest graduation with glass wool. Three mL of dry sorbent were then poured into the tube and packed by gentle tapping. Another layer of glass wool was packed on top of the sorbent. The sorbent tube pipet was connected to the pumping system via a 5/16 inch to 1/4 inch stainless steel Swagelok reducing union with teflon ferrules or a 5/16 inch Swagelok - NPT tee with connection to a NPT 1/4 inch Swagelok union. Due to the irregularities in the pipets, it was necessary to slightly enlarge the inside diameter of the 5/16 inch Swagelok connection by drilling. The assembled sorbent samping tube is shown schematically in Figure 5.

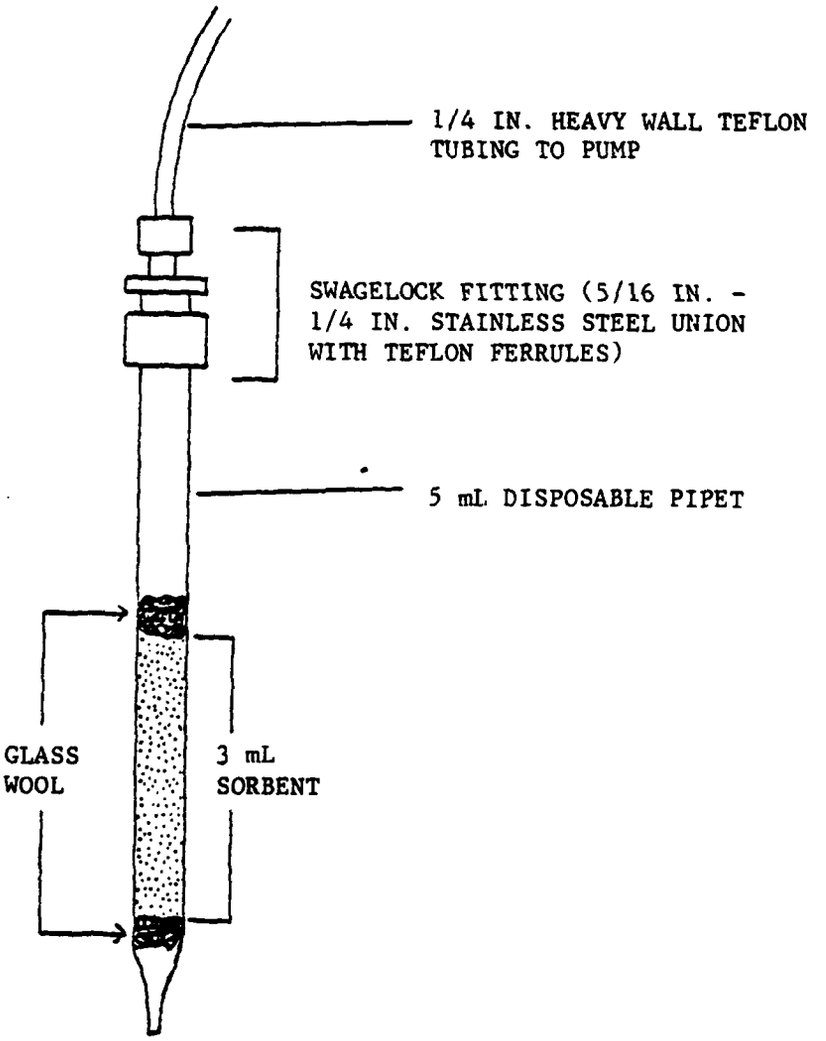


Figure 5. Sorbent Sampling Tube Design

Connection of the sorbent tube to the pumping system and of the pumping system to the sample reservoir was accomplished by 1/4 inch O.D. heavy wall teflon tubing. This type of tubing was chosen because it is chemically inert, free of plasticizers and flexible, yet sufficiently rigid to be suitable for use with Swagelok fittings. The pump chosen for the system was a FMI-Lab model SS50-1296 metering pump which was capable of reproducible pumping rates infinitely adjustable from 0 to approximately 1 liter/hour (depending upon the back pressure experienced).

2. Desorption Apparatus

The apparatus requirements for desorption are more variable than those for adsorption. Desorption can be accomplished in much the same manner as adsorption, i.e. simply by pumping the desorption solution through the tube in the same manner that the water sample was pumped. This technique has the advantage that a controlled rate of solvent flow can be maintained but has the disadvantage that the pumping system is tied up during desorption and that only one tube can be desorbed at a time per pump.

An alternative desorption method is gravity flow desorption, where the solvent is added above the sorbent and allowed to drain naturally through the tube. This technique can be modified by manual application of pressure with an "autopipet" bulb. No additional apparatus is required for this desorption technique.

For other possible desorption techniques, however, additional apparatus may be required. One possible option is the use of a heating jacket to control the temperature of the sorbent tube during desorption. For this option, a small water jacketed distillation condenser was chosen which had an inside tube diameter as close as possible to the O.D. of the sorbent tube (5/16 inch). For temperature control, water of the desired temperature can either be pumped through the condenser or the condenser can be filled with water, closed with a length of teflon tubing (also filled with water) and heated with a heating tape.

Another option is reverse desorption or desorbing in the direction opposite from adsorption. If desorption is performed with the pumping system, the tube need only be reversed in the 5/16 inch Swagelok fitting. For gravity desorption or manually assisted gravity desorption the following apparatus was designed. A section of 5/8 inch teflon tubing was drilled out to 5/16 inch to accomodate both the reversed sorbent tube and an empty 5 mL disposable pipet from which the tip had been removed. This system allowed for a solvent head of at least 5 mL above the sorbent as shown in Figure 6.

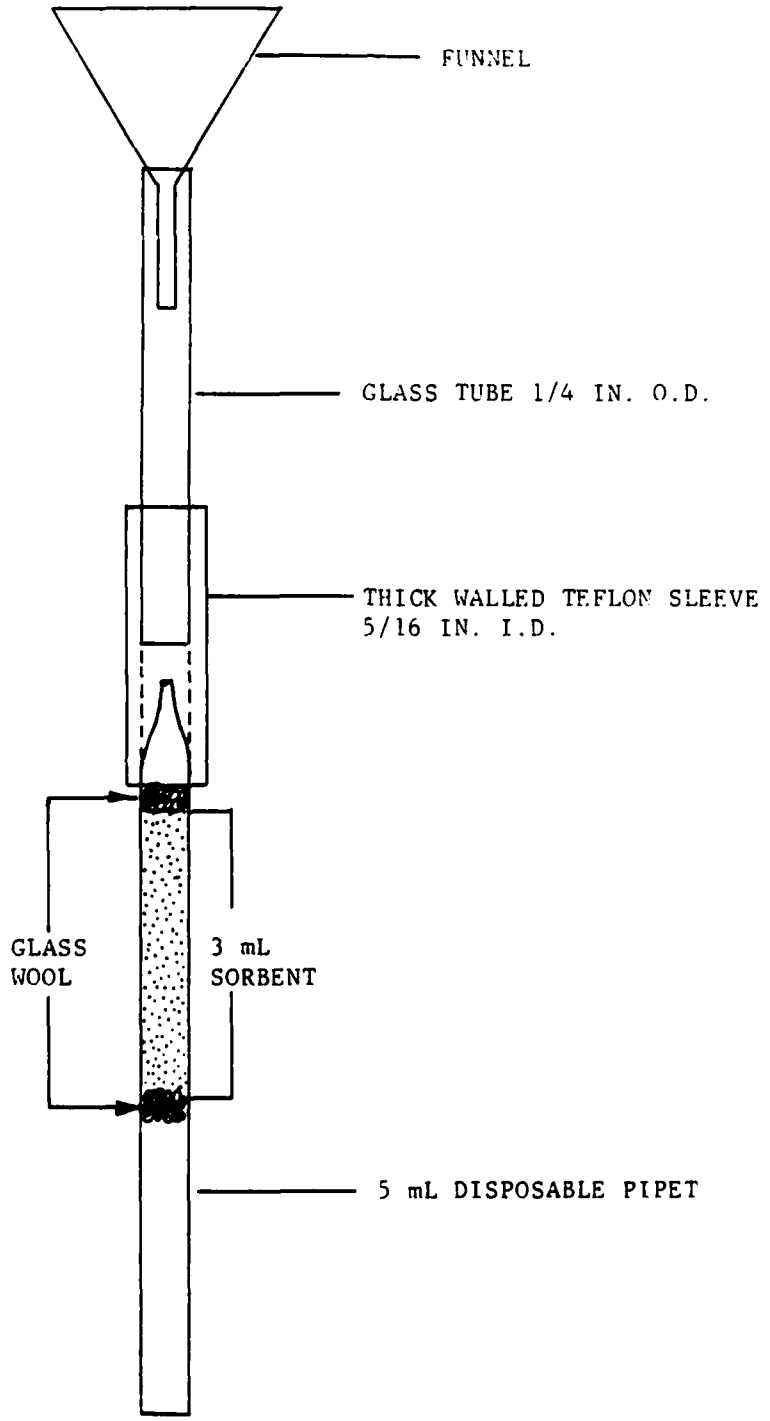


Figure 6. Gravity Flow Desorption Apparatus Tube

B Sorbent Evaluation Methodology

This section outlines the general procedures used to screen the sorbents for their ability to efficiently adsorb and desorb the explosives of interest, optimization of the sorbent/analytical procedure, precision and accuracy testing of the methods and preservation studies on the loaded sorbent tubes.

1. Methods Development for Low Level Explosives in Water

Before any experimental work was conducted with the explosives and various sorbents, analytical techniques for quantitating low levels (less than 10 µg/L) of the explosives in water were developed. The analytical procedures were obtained either from past studies performed by Atlantic Research Corporation, other USATHAMA contractors, or the general literature. Each method was perfected in the laboratory and subjected to USATHAMA quality control procedures to determine the detection limit, precision and accuracy of the method. This quality control procedure involved analysis of six samples of specified concentration ratios (0, 0.5, 1, 2, 5 and 10 DL where DL is the specified detection limit) on each of four consecutive days. The data were analyzed by the method of Hubaux and Vos (1975) to determine the detection limit and precision and accuracy. The analytical methods developed for the explosives in water and the detection limits are listed in Table 20. The complete methods are compiled in Appendix B. No suitable methods were found for picric acid, tetrazene, or lead styphnate after an extensive search of the literature. The methods found either were not specific for the explosive or did not have the required detection limit.

2. Preparation of Sorbents

The literature contains many references to interferences observed in analyses due to monomer and other compounds retained on the sorbent from the manufacturing processes. In our laboratory evaluation of the different sorbents, we found interferences from these unwanted contaminants to be a major problem. The problem of sorbent contaminant interferences was especially pronounced when HPLC is used with detection at wavelengths below 230 nm.

Two methods of cleaning the sorbent were investigated - pumping the intended desorbing solvent, e.g. acetone, through the packed sorbent tube and soxhlet extraction of the sorbent before loading the tubes. Soxhlet extraction of the sorbent with acetone for 2 hours yielded sorbent of sufficient quality for gas chromatographic analysis of the desorbed material. However, if the desorbed material was to be analyzed by HPLC at wavelengths less than 230 nm, soxhlet extraction alone did not sufficiently clean the sorbent. To clean sorbents for HPLC analysis, large volumes (approximately 500 mL) of acetone were pumped through the tubes which were packed with soxhlet extracted sorbent (see Section IIIA for packing methodology). The acetone was analyzed periodically for contaminants and the washing procedure was continued until the acetone was contaminant-free.

Table 20. Methods for Analysis of Explosives in Water

Explosive	Method	USATHAMA Approval No.	Detection Limit
2,4-DNT	GC-EC	1A	0.91 µg/L
2,6-DNT	GC-EC	1A	0.81 µg/L
TNT	GC-EC	1A	0.85 µg/L
RDX	HPLC	6B	7.5 µg/L
Tetryl	GC-EC	1A	5.3 µg/L
Nitroglycerine	HPLC	6B	8.1 µg/L
PETN	HPLC	6B	10.3 µg/L

Once the contaminants had been removed from the sorbent, the glass pipet sorbent tubes were loaded according to the procedure discussed in Section IIIA. The columns were then activated by pumping 50 mL of HPLC methanol or acetone and 50 mL of distilled water through the tubes. The tubes were labeled and wrapped in aluminum foil to help the sorbent retain its moisture and stored in a refrigerator until ready for use.

3. Sorbent Deletion/Screening

The purpose of the screening experiments was to eliminate those sorbents which were unacceptable due to their inability to trap the explosive in question from water. To reduce the number of experiments required to accomplish this task, the list of explosives was subdivided into 6 categories, as shown in Table 21. Screening was performed on only one explosive from each category as identified by an * in the table. Screening tests were conducted with those sorbents listed in Table 22. In some of the earlier screening studies, certain sorbents were not included in the screening procedures because of delays in shipping from the manufacturer. As the program progressed, certain sorbents were repeatedly shown to have undesirable characteristics (e.g., dissolved in the elution solvents) and were eliminated from the screening procedures.

Screening experiments presented a difficulty for which some compromise was necessary. Since the conventional detection limits for the explosives are in the range of 1 to 10 µg/L (which is the same range to which the ultimate solid sorbent techniques were to be applied), we had a choice between two less than ideal options. The first option would be to do screening on solutions spiked in the 1 to 10 µg/L range. This option would allow leakages of from 10-50% of the spike without the explosive being detectable. Alternatively solutions spiked at much higher levels of explosives could be used. This option would allow for more convenient and accurate analysis but was unrealistic relative to the ultimate experiment. The decision was made to proceed with the second option since leakage through the sorbent tube would be easily detectable. It was also reasoned that a sorbent tube capable of efficiently trapping high levels of exlosives from water would also effectively trap the low levels.

Screening experiments were performed by passing a total of 100 mL of approximately 1 mg/L aqueous solution of the subject explosive through an array of sorbent tubes. The aqueous filtrates from the sorbent tubes were collected and analyzed according to the methods listed in Table 20. The amount of explosive in the effluents was compared to that introduced onto the tube to calculate the percent leakage of the explosive through the sorbent column. Only sorbents which showed less than 5% leakage of the explosive through the column were considered for further testing.

Table 21. Grouping of Explosives for Screening of Sorbents

A. Nitroaromatics
   - TNT
   - 2,4-DNT
   - 2,6-DNT*

B. Nitramines
   - RDX
   - Tetryl*

C. Nitrate Esters
   - PETN
   - Nitroglycerine*

D. Picric Acid*

E. Tetracene*

F. Lead Styphnate

Table 22. Characteristics of Sorbents Evaluated in Screening Studies

Sorbent	Type	Particle Size	Specific Surface Area m^2/g	Average Pore Diameter nm
XAD-2	SDVB	20/60	300	9
XAD-4	SDVB	20/60	725	4
XAD-7	Acrylic Ester	20/60	450	9
XAD-8	Acrylic Ester	20/60	160	22.5
Chromosorb 104	ADVB	80/100	100	60
Porapak R	Vinyl Pyrrolidone	100/120	780	7.6
Porapak S	Vinyl Pyrrolidone	100/120	670	7.6
XE-340	Carbonaceous	20/60	400	10
XE-347	Carbonaceous	20/60	350	10
XE-348	Carbonaceous	20/60	500	10
C-18	on silica	60/200	-	-
C-18	on silica	200/325	-	-
C-18	on silica	40	-	-

SDVR - styrene divinylbenzene
ADVR - acrylonitrile divinylbenzene

4. Desorption Studies

The sorbents that passed the initial screening tests for each explosive were then subjected to desorption studies. The desorption experiments were conducted in the following manner. The explosives in each group were combined in an aqueous solution containing approximately 1 mg/L of each explosive. One hundred mL of this solution was pumped through the sorbent tubes. After the tubes were loaded and allowed to drain, desorption were accomplished by pumping two 10 mL aliquots of acetone (or other solvent) through each tube. A solvent interface was observed to elute with the first acetone fraction. Thus even though the tubes were allowed to drain, a significant quantity of water was retained on the sorbent. The water preceeding the solvent front was discarded and only the acetone fractions were collected for analysis. The percentage recoveries of the explosives were determined by comparing the quantity of explosives in the acetone eluate with that placed on the sorbent.

5. Optimization Studies

During the optimization studies, various methods of loading and desorbing the sorbent tubes and analysis of the eluate were evaluated. In the optimization studies, a liter of water containing approximately 10 µg/L of the explosive was pumped through the sorbent tubes to simulate actual field collection conditions. Each sorbent/explosive combination had its own unique problems which were investigated so that the procedures could be optimized to give the most efficient and reliable results. The specific procedures used in the optimization studies are described along with the results in Sections IIIC - IIIG.

6. Analytical Method Detection Limit and Precision and Accuracy

Once the solid sorbent procedures were optimized, the detection limit and precision and accuracy of each procedure were determined by analyzing six samples on each of four consecutive days according to the procedures set forth by the USATHAMA QC Plan. The six samples consisted of a blank, and the following specified concentrations: 0.5 DL, 1 DL, 2 DL, 5 DL, and 10 DL (where DL is the expected detection limit). The resulting data were analyzed by the method of Hubaux and Vos (1975). Each solid sorbent technique was deemed acceptable only if the detection limit of the explosive in water was less than 10 µg/L and the correlation coefficient for the data was greater than 0.99. The complete methodology and detection limit data for each solid sorbent/-explosive method developed under this contract are presented in Section IV.

7 Preservation Tests

For solid sorbent sampling tubes to be of value for field use, the explosives adsorbed onto the resin must remain stable until desorption and analysis can be performed. To evaluate the stability of the explosives on the various sorbents, the effects of the following storage conditions were determined:

- wet resins versus resin dried by a tream of nitrogen
- dark (foil wrapped) versus light (exposure to sunlight for 1 week)
- cold (4°C in refrigerator) versus warm (70°C constant temperature)
- sealed (glass sealed by a flame) versus unsealed

For each storage condition, triplicate sorbent tubes were loaded with the approximate 5 DL level of explosive(s) and subjected to the appropriate environment. After the initial studies with TNT and the DNT's, it was apparent that storage in sunlight was totally unacceptable. Sealing the ends of the tube versus open tubes and wet versus dry had little affect on the recovery, therefore, only cold and room temperature storage conditions were evaluated. After the tubes were loaded, they were foil wrapped and stored in a refrigerator at 4°C or at room temperature (70°C) for a period of 3 weeks. Desorption and analysis were performed according to the methods in Appendix C.

C. Development of a Solid Sorbent Method for Analysis of 2,4-DNT, 2,6-DNT and TNT in Water

1. Screening Studies

2,6-Dinitrotoluene was used as the test compound for sorbent screening studies for the nitroaromatic group of explosives. The results of the screening studies of the various sorbents with 2,6-DNT are presented in Table 23. All analyses were performed by gas chromatography-electron capture according to USATHAMA approved Method No. 1A. As can be observed from the table, most of the sorbents were effective in adsorbing the 2,6-DNT. Notable exceptions were the C-18 on silica, XE-340 and XAD-7 which showed leakages ranging from 10% to massive breakthrough. These sorbents were eliminated from further evaluation for the nitroaromatics. Even though substantial leakage occurred with the XAD-4, it was included in the desorption studies based on literature data which indicated good recoveries of nitroorganics from this resin.

Table 23. Sorbent Screening Studies with 2,6-DNT*

Sorbent	Concentration of 2,6-DNT in Filtrate	% Leakage
XAD-4	30.7 µg/L	3.07%
XAD-7	100.5 µg/L	10.0%
XAD-8	< 0.81 µg/L	< 0.081%
XE-340	Massive Leakage	
Porapak R	< 0.81 µg/L	< 0.081%
Porapak S	< 0.81 µg/L	< 0.081%
Chromosorb 104	< 0.81 µg/L	< 0.081%
C-18 on Silica (60/200)	Massive Leakage	
Charcoal 60/80	< 0.81 µg/L	< 0.081%
Filtersorb 300	< 0.81 µg/L	< 0.081%

* 100 mL of an aqueous solution (standard water) containing 1 mg/L of 2,6-DNT was passed through each tube. Analysis was accomplished by GC-EC Method No. 1A.

2. Desorption Studies

Several of the sorbents were not available when the initial screening studies were performed with 2,6-DNT (e.g., XAD-2, XE-347, XE-248, and Cyano Baker and C-18 Baker). These sorbents were included in the desorption tests to determine their suitability for sampling the nitroaromatics from water. The desorption studies were performed by passing 100 mL of water containing 1 mg/L of 2,6-DNT, 1 mg/L of 2,4-DNT and 1 mg/L of TNT through tubes containing the various sorbents. After the tubes were loaded, each tube was desorbed with two 10 mL aliquots of acetone and the acetone eluate analyzed. The results are presented in Table 24.

Recoveries of the nitroaromatics from the XAD and Porapak resins, the Chromosorb 104 and the C-18 Baker all averaged about 50-67%. In contrast, the carbons and carbonaceous resins and Cyano Baker showed poor recoveries of all the nitroaromatics. From these data, four resins were chosen for optimization studies to determine if the desorption efficiency could be improved. The sorbents chosen, Porapak S, XAD-4, Chromosorb 104 and Baker C-18, were selected on the basis of best overall recovery for all three explosives. XAD-2 was eliminated from further consideration because of its similarity to XAD-4 and better recoveries were found with XAD-4. Porapak S was chosen over Porapak R for the same reasoning. The selection of Chromosorb 104 over XAD-8 was somewhat arbitrary and was primarily based on the high recovery of TNT from the Chromosorb 104 resin.

3. Optimization Studies

The initial optimization experiments on the four resins were carried out by pumping one liter of an aqueous solution containing TNT, 2,4-DNT and 2,6-DNT through previously activated sorbent tubes. The aqueous solution of the explosives was prepared from standard water (distilled water containing 100 mg/L each of sulfate and chloride) and contained 10 µg/L of each explosive. The loaded sorbent tubes were desorbed by pumping acetone through each tube and collecting two 5 mL fractions without any attempt to discard the initial water fraction. Desorptions on each sorbent were run both "wet" and "dry" in an effort to investigate the effect of pre-drying the sorbent tube. The "dry" tubes were prepared by blowing dry nitrogen through the loaded sorbent tubes for several minutes dry or until all evidence of residual water had been eliminated.

The results of this initial optimization study are shown in Table 25. Data in the table reflect the percentage of the original spike recovered both: 1) in the water filtrate and 2) in the combined acetone eluates of the sorbent. Several observations can be made from the results obtained. First, it is apparent that the Baker C-18 cartridges are inadequate for use with 1 liter volumes of water. Although previous results demonstrated sufficient capacity to trap the

Table 24. Adosrption/Desorption Recoveries (%) for 2,6-DNT, 2,4-DNT and TNT*

	TNT+		2,6-DNT+		2,4-DNT+		Average Overall Recovery (percent)
	1st	2nd	1st	2nd	1st	2nd	
XAD-2	47.8	3.1	58.3	7.8	65.8	4.6	62.5
XAD-4	55.2	3.08	62.5	9.6	55.6	8.8	64.9
XAD-8	45.4	4.5	57.5	-	63.6	4.3	58.4
XE-347	2.3	0.9	3.5	6.3	3.1	3.4	6.5
XE-348	0.6	0.91	3.5	5.9	1.4	-	4.1
Porapak R	67.2	14.0	57.4	3.7	38.8	0.3	60.5
Porapak S	59.7	0.6	59.9	4.9	65.1	0.5	66.9
C-18 Baker	83.5	0.4	52.6	0.8	53.2	1.1	63.9
Cyano Baker	26.5	0.4	6.5	2.6	3.7	0.0	13.2
Filtersorb 300	3.4	0.8	19.9	13.7	1.8	2.0	13.9
Charcoal 60/80	0.6	0.5	2.2	1.8	0.2	0.6	2.0
Chromosorb 104	77.3	0.4	51.9	1.7	44.0	1.2	58.8

* 100 mL of an aqueous solution (standard water) containing 1 mg/L of TNT, 2,4-DNT and 2,6-DNT passed through each tube

+ Percent recovery of first and second acetone eluates; analysis by GC-EC Method 1A or modification thereof.

- sample not analyzed

Table 25. Initial Optimization Studies for TNT, 2,4-DNT and 2,6-DNT*

	% Original Spike			
	Dry		Wet -	
	Water Filtrate	Acetone Eluate	Water Filtrate	Acetone Eluate
2,4-DNT				
Sorbent				
Porapak S	0.0	44.6	0	52.4
XAD-4	6.21	45.1	3.76	41.8
Chromosorb 104	1.6	37.7	3.0	39.4
Baker C-18	44.4	12.2	42.3	9.91
2,6-DNT				
Porapak S	0.5	113	0.0	104
XAD-4	0.0	38	0.8	36
Chromosorb 104	0.0	50	0.0	104
Baker C-18	105	13.8	13.8	7.1
TNT				
Porapak S	1.7	14.8	2.2	11.8
XAD-4	1.5	18.4	2.2	17.4
Chromosorb 104	2.95	13.7	1.6	10.7
Baker C-18	59.1	3.3	60.1	2.1

* One liter of aqueous solution (standard water) containing 10 µg/L of each explosive was passed through each tube; analysis of filtrates and eluates was by GC-EC by Method 1A or modification thereof.

quantities of explosives involved in this experiment, the total volume of liquid pumped through the cartridges never exceeded 100 mL. The present data, however, clearly illustrates that that explosives were in fact not "trapped" but were slowly eluting from the sorbent tubes. The second observation which can be made is that there is little apparent differences between tubes that were blown dry rather than simply drained. Thus, either water has no adverse effect on the process or blow drying is no more effective for water removal than gravity drainage.

The data indicate that Porapak S was slightly superior to the other resins when overall results for the three explosives were taken into consideration. XAD-4 gave the best results for TNT but was less effective with the DNT's. Chromosorb 104, yielded recoveries comparable to Porapak S and XAD-4, however, a significant portion of the resin dissolved in the acetone. After repeated injections on the GC column, the dissolved Chromosorb 104 interfered with the GC separation of the nitrotoluenes. Chromosorb 104 was thus eliminated from further consideration. Based on these data, Porapak S was selected as the only sorbent to be included in further optimization studies.

The most striking observation that can be made from the data in Table 25 was the extraordinary low recoveries obtained for TNT. The TNT recoveries were much worse than those obtained in the previous desorption experiments despite the lack of any obvious experimental differences which could be responsible for the low recoveries. The major difference in the two experiments was that the desorption study involved a total water volume of 100 mL compared to the 1 liter of solution employed in the optimization studies. The possibility existed that adsorption over the longer period of time necessary to pass one liter of water through the sorbent tube could result in either decomposition of the TNT or allow the TNT to become more permanently adsorbed within the microporous structure of the sorbent rather than hydrophobically adsorbed on the surface.

To further investigate these possibilities and investigate other potential desorption techniques, a series of additional optimization studies were performed with TNT and Porapak S. These experiments included an investigation of the effects of light, heat and alternative desorption solvents and techniques on the recovery of TNT. In an experiment in which the sorbent tube (as well as the stock solution) were wrapped in foil to eliminate the possibility of a light induced decomposition of the TNT, the recovery was in fact worse than that obtained without these precautions. Desorption experiments employing acetone as the initial eluant followed by benzene gave variable results, but in all cases the majority of the recovery was from the acetone eluate rather than the benzene. An experiment employing a combination of acetone and diethyl ether eluant resulted in essentially zero recovery. Attempts to employ the previously described heated condenser jacket desorption technique also failed to yield improved results.

It was imperative at this point to determine whether in fact the TNT was adsorbed on the sorbent tubes and where it was adsorbed. In separate experiments, the contents of one loaded sorbent tube (Porapak S/TNT) were divided into three equal portions and each portion extracted manually by shaking with 5 mL of acetone. The entire contents of a second tube were extracted with 54 mL of acetone in a soxhlet extractor. The results of the divided tube experiment showed that 91% of the TNT recovered was located in the upper third of the sorbent in the tube. Both the divided tube and soxhlet extraction experiments gave good overall recoveries (80-90%). Attempts to test the reproducibility of either the manual extraction or soxhlet extraction techniques gave generally high but quite variable recoveries. The problems in reproducibility appeared to be related to difficulties in emptying the sorbent tubes without loss of sorbent and a tendency of the sorbent to soak up the acetone.

Throughout the course of these experiments, it had been noted that an overall loss of GC sensitivity was observed for standards run after a series of desorption samples relative to standards run before the desorption samples. Also, it was observed that samples which were diluted in benzene prior to analysis generally gave higher results (after application of the appropriate dilution factor) than undiluted samples. This finding suggested that the low recoveries were in fact caused by the presence of water in the samples which lowered the sensitivity of the electron capture detector. In the original desorption experiments, most of the residual water was discarded as the fraction preceeding the solvent interface. In the soxhlet and manual extraction experiments, the volume of acetone was much larger relative to the amount of sorbent extracted thus making the water concentration less. Also, samples which had been diluted in benzene contained a significantly lower concentration of residual water.

The final technique tested took advantage of as many of the above observations as possible. The technique utilized a slow manually assisted gravity flow desorption over a period of approximately 15 minutes. To take advantage of the fact that the majority of explosive is located in the upper third of the tube, the tube was inverted and desorption carried out in the reverse direction. Ten mL of acetone were used as the eluant allowing collection of approximately 7.5 mL of eluate. Finally, to avoid problems associated with residual water, each sample was first diluted 1:5 with benzene and dried with anhydrous sodium sulfate prior to analysis. To determine if this technique would yield reproducible results, two Porapak S tubes were loaded with one liter of a 5.20 µg/L aqueous TNT solution and desorbed using the reverse desorption technique. The results, shown in Table 26, show a relatively consistent 82% recovery. The porapak S using the reverse desorption technique was then subjected to USATHAMA four-day precision and accuracy testing. The results of this testing are presented in Section IVA.

Table 26. Final Optimization Study with TNT*

		µg Recovered	% Recovery
Sample	#1	4.28	82.3
	#2	4.27	82.1

*One liter of aqueous solution (standard water) containing 5.20 µg/L of TNT was applied to each sorbent tube. Desorption was accomplished by inverting the tubes and allowing the acetone eluant to gravity flow through the tubes.

D. Development of a Solid Sorbent Method for Analysis of RDX and Tetryl in Water

1. Screening Studies

Tetryl was used as the model compound to screen the various sorbents for their ability to adsorb the nitramine explosives. The screening study results are presented in Table 27. The data indicate acceptable adsorption (less than 5% leakage) for XAD-4, XE-347, XE-348, Porapak S, Porapak R, and Chromosorb 104. Due to the previously experienced problems associated with the dissolution of Chromosorb 104 in the desorption solvents, this resin was eliminated from further consideration.

2. Desorption Studies

Desorption studies were carried out by passing two 10 mL portions of acetone through sorbent tubes previously loaded with tetryl or RDX. The two compounds were studied separately because of the different analytical methods employed (GC-EC for tetryl and HPLC for RDX). Since RDX is usually found in association with TNT, it was hoped that the sorbents found to be best for TNT (Porapak S or alternatively XAD-4) would also be satisfactory for RDX. Therefore, these two resins were evaluated first. The data from the RDX desorption studies with Porapak S and XAD-4 are presented in Table 28. Although XAD-4 showed good recovery of RDX, recoveries from Porapak S were essentially quantitative. Thus, Porapak S was selected for optimization studies with RDX.

Table 27. Sorbent Screening Studies with Tetryl*

Sorbent	Concentration of Tetryl+ in Column Filtrate	% Leakage
XAD-2	178 µg/L	13.4
XAD-4	45 µg/L	3.38
XAD-8	134 µg/L	10.1
XE-340	Massive Leakage	54
XE-347	40 µg/L	3.0
XE-348	52 µg/L	3.9
Porapak S	2.4 µg/L	0.18
Porapak R	25 µg/L	1.85
Chromosorb 104	0	0
C-18 on Silica (60/200)	Massive Leakage	86
Baker C-18	Massive Leakage	59

* 100 mL of an aqueous solution (standard water) containing 1.33 mg/L of tetryl were passed through the tube.

+ Analysis was by GC-EC according to Method No. 1A.

Table 28. Adsorption/Desorption Recoveries for RDX*

		µg Recovered	% Recovery
XAD-4	#1	7.266	70.1
	#2	9.576	93.3
Porapak S	#1	10.525	101.5
	#2	9.946	95.9

* 100 mL of an aqueous solution (standard water) containing 103.7 µg/L of RDX were loaded onto the sorbent tubes. Analysis was by HPLC according to modified Method No. 1A.

In contrast to the RDX data, the recoveries of tetryl from all of the sorbents were negligible (less than 5%). It was not immediately clear whether the problem was one of strong affinity of tetryl to the sorbents leading to difficulty in desorption or decomposition of tetryl either in stock solutions, on the sorbent, on the GC column or in the extract. There have been numerous, but non-reproducible, indications observed in this laboratory of problems with respect to the stability of tetryl in certain solvents such as methanol or acetone. However, re-examination of several of the sorbent tubes three weeks after the attempted desorption showed that discoloration of the tubes had occurred, indicating that the tetryl had in all likelihood not been removed from the sorbent. The discoloration was most intense at the top of the tube as would be expected. On the basis of this information, it was decided that an alternative desorption technique and/or solvent was needed.

3. Optimization Studies for RDX

Optimization studies on RDX were performed by passing a liter of an 8.27 µg/L solution of RDX through Porapak S sorbent tubes. The tubes were desorbed with a 10 mL portion of acetone and the eluate analyzed by HPLC according to a modified version of Method No. 6B. The results are shown below:

		µg Recovered	% Recovery
Porapak S	#1	8.55	103
	#2	8.50	103
	#3	8.70	105

As can be seen, the recoveries were essentially quantitative and quite reproducible. Since Porapak S has been chosen as the sorbent of choice for both RDX as well as TNT and the isomeric DNT's, it was decided to include RDX in the 4-day precision and accuracy testing along with the nitrotoluenes.

4. Optimization Studies for Tetryl

For the purpose of improving the negligible recoveries obtained for tetryl, it was decided to employ benzene as an alternative desorption solvent and to use the reverse desorption technique since the majority of the tetryl was sorbed at the top of the column. To insure contact of the benzene with the tetryl adsorbed onto the resin, one mL of methanol was feed through the column ahead of the benzene eluant.

Optimization experiments were performed on two sorbents in duplicate, Porapak S and XAD-4. Each sorbent tube was loaded with 100 mL of a water solution containing 2.66 µg/L of tetryl. Desorption was accomplished by drying each tube in a stream of nitrogen and inverting it into the reverse desorption apparatus. One mL of methanol was added and forced through the column with a rubber bulb. Finally, 10 mL of benzene were added and allowed to gravity drain through the column. From five to seven mL of eluate were collected. The benzene layer was separated from the water/methanol layer by centrifugation and analyzed by GC-EC Method No. 1A. The results, based on 6.5 mL of benzene extract were:

		µg Recovered	% Recovery
XAD-4	#1	198	74.5
	#2	2.31	87.0
Porapak S	#1	1.30	48.9
	#2	1.52	57.2

An average of 81% recovery was considered to be sufficiently high to warrant proceeding with precision and accuracy testing with XAD-4.

E. Development of a Solid Sorbent Method for Analysis of Nitroglycerine and PETN in Water

1. Sorbent Screening

Screening studies for nitroglycerine and PETN were performed using nitroglycerine as the representative compound. One hundred mL of a 3.1 mg/L solution of nitroglycerine was pumped through each sorbent. The eluate was analyzed via HPLC according to the method in Appendix B. The results, shown in Table 29, are expressed as a percent of the original spike. As can be seen, most of the sorbents, with the possible exception of the reverse phase C-18 packings and the Baker Cyano cartridges, gave acceptable performances. The C-18 and Baker cyano sorbents were eliminated from further study.

2. Desorption Studies

For the desorption studies, 100 mL of an aqueous solution (standard water) containing 3.1 mg/L of nitroglycerine or 3.40 mg/L of PETN were pumped through the sorbent tubes. Desorption was accomplished by pumping two 5 mL portions of actone through the sorbent tubes. The acetone eluates were then blown to dryness under a stream of nitrogen and reconstituted in 5 mL of HPLC hexane. Analyses were performed by HPLC according to a modification of Method No. 6B.

The data obtained in the desorption studies are presented in Table 30. Due to instrumental difficulties (an out of range situation on the strip chart recorder, and malfunctioning of the electronic integrator), the larger values in the PETN study are unreliable and should be considered as a lower limit only. The nitroglycerine values were, therefore, the major factor considered in the selection of sorbents to be subjected to optimization studies. As can be observed from the nitroglycerine data, excellent desorption results were obtained with XAD-4. Porapak R, XE-340 and XAD-7 also yielded acceptable results. Therefore, it was decided to proceed with the optimization studies with these four sorbents.

Table 29. Sorbent Screening Studies With Nitroglycerine*

Sorbent	Concentration of Nitroglycerine in Column Filtrate	% Leakage
XAD-2	12.3 µg/L	0.39
XAD-4	4.4 µg/L	0.14
XAD-7	0	0
XAD-8	1.5 µg/L	0.05
XE-340	21.8 µg/L	0.69
XE-247	4.4 µg/L	0.14
XE-348	2.2 µg/L	0.07
Porapak R	2.9 µg/L	0.09
Porapak S	0.8 µg/L	0.03
C-18 on Silica (60/200)	34.6 µg/L	1.10
C-18 on Silica (200/325)	18.1 µg/L	0.57
Charcoal 60/80	2.2 µg/L	0.07
Filtersorb 300	4.4 µg/L	0.14
Chromosorb 104	4.4 µg/L	0.14
Baker Cyano	145.0 µg/L	4.58
Baker C-18	32.6 µg/L	1.03

* 100 mL of an aqueous solution (standard water) containing 3.168 mg/L of nitroglycerine were pumped through the sorbent tubes. The aqueous filtrate was analyzed by HPLC according to Method No. 6B.

Table 30. Nitroglycerine and PETN Desorption Studies*

Sorbent	Nitroglycerine µg Recovered	Nitroglycerine % Recovery	PETN+ µg Recovered	PETN+ % Recovery
XAD-2	38.1	1.2	523	15.4
XAD-4	2630.0	83.0	694	20.4
XAD-7	1260.3	39.8	454	13.4
XAD-8	29.7	0.9	463	13.6
XE-340	1609.5	50.8	1051	30.9
XE-347	Contaminated		807	23.7
XE-348	203.2	6.4	680	20.0
Porapak R	1680.0	53.0	426	12.5
Porapak S	557.0	17.6	456	13.4
Charcoal 60/80	63.0	2.0	1202	35.4
Filtersorb 300	32.0	1.0	438	12.9
Chromosorb 104	308.0	9.7	1344	39.5

* 100 mL of an aqueous solution (standard water) containing 3.168 mg/L of nitroglycerine or 3.40 mg/L of PETN were pumped through the sorbent tubes. The tubes were desorbed with two 10 mL volumes of acetone, the acetone blown dry under nitrogen and the sample reconstituted in 5 mL of HPLC hexane for HPLC analysis.

+ PETN numbers are only a lower limit due to instrumental difficulties.

3. Optimization Studies

Three desorption techniques were chosen for evaluation in the optimization studies for nitroglycerine and PETN. The normal procedure "C" employed was the gravity desorption with two 5 mL portions of acetone. A modification of this procedure, "B" was a gravity desorption with one 5 mL portion of acetone followed by a 5 mL portion of methylene chloride. In the third technique, "A", the sorbent was removed from the column and transferred to a centrifuge tube. Five mL of acetone were added to the tube, the contents shaken, centrifuged and decanted. This extraction procedure was repeated with a second 5 mL portion of acetone and the extracts combined.

In the initial experiments, the sorbents (XAD-4, XAD-7, XE-340 and Porapak-R) were loaded by pumping one liter of a standard water containing 5.27 µg/L nitroglycerine and 6.06 µg/L PETN through each tube. The data from the initial experiments are presented in Table 31. The best combined results for both explosives was obtained using the normal "C" acetone desorption with Porapak R. Porapak R was subjected to precision and accuracy testing for determining nitroglycerine and PETN from water.

F. Development of a Solid Sorbent Method for Analysis of Picric Acid in Water

1. Screening Studies

For the screening studies, 100 mL of a 1.04 mg/L solution of picric acid in standard water were pumped through a selected series of sorbent tubes. The sorbent tubes evaluated were selected on the basis of the results obtained in screening other explosives and that reported in the literature on other phenolic compounds. The column filtrate was analyzed by HPLC according to the following procedure. A Perkin-Elmer Model 602 LC with an L55 variable wavelength spectrometric detector, a LC420 autosampler and a Waters (10 cm x 7 mm) radical compression column was used for the analysis. The column was packed with 10 micron ODS reverse phase packing. The carrier solvent was 50% acetonitrile, 50% water, made to 0.005M with tetrabutylammonium hydroxide and buffered to 6.5 with phosphoric acid. Solvent flow rate was 2.0 mL/min. UV detection at 205 nm was employed. This wavelength was chosen based on the UV spectrum of picric acid complexed with tetrabutylammonium hydroxide. Samples were injected directly onto the HPLC column with no previous concentration. The detection limit for this method is less than 25 µg/L, however, four-day precision and accuracy testing was not performed.

Table 31. Optimization of PETN/Nitroglycerine Desorption Procedure*

Sorbent	Procedure	Nitroglycerine µg Recovered	Nitroglycerine % Recovery	PETN µg Recovered	PETN % Recovery
XAD-4	A	4.48	85	4.32	65
	B	2.31	44	3.05	46
	C	2.98	57	8.36	126
XAD-7	A	0.65	12	0.5	8
	B	3.48	66	4.96	74
	C	7.47	142	2.94	44
XE-340	A	0.32	61	2.2	33
	B	4.31	82	6.45	97
	C	3.98	76	5.6	84
Porapak R	A	2.77	53	2.18	33
	B	4.31	82	5.9	89
	C	5.34	101	6.11	92

*One liter of a solution containing PETN (6.06 µg/L) and nitroglycerine (5.27 µg/L) was pumped through XAD-4, XAD-7, XE-340, and Porapak R sorbent tubes. Desorption was accomplished by the following procedures:

A. dump sorbent into test tube and extract with two 5 mL portions of acetone.

B. desorb with 5 mL of acetone followed by 5 mL CH_2Cl_2.

C. desorb with two 5 mL portions of acetone.

The results of the screening study are compiled in Table 32. Of the sorbents evaluated only XE-348 and Porapak R showed acceptable adsorption of the picric acid.

2. Desorption Studies

The available literature data on desorption of phenols from water indicate very low desorption efficiencies. Evidently the phenols are either tightly bound to the resins or undergo decomposition on the resins. Desorption studies were carried out with two resins, Porapak R and XE-348. The tubes were loaded with 100 mL of a 1.04 mg/L aqueous picric acid solution. Desorption was accomplished with methanol, and methanol containing 0.05M tetrabutylammonium hydroxide. Methanol was chosen as the desorption eluant since it can be injected directly into the HPLC. Tetrabutyl ammonium hydroxide was added in the hope that it would complex with the picric acid and allow it to be removed from the resin. Ten mL of the eluants were added to the loaded columns. The eluate (7.5 mL) from each column was collected and diluted to 20 mL with distilled water. Two drops of 1M phosphoric acid were added and the sample was injected into the HPLC using the same conditions as described under the screening studies.

Recovery of picric acid from Porapak R was less than 10% with methanol as the eluant. When methanol containing 0.05M tetrabutylammonium hydroxide was used as the eluant, 50.4% of the picric acid was recovered. No detectable amounts of picric acid were recovered from desorption of XE-348 with either eluant.

3. Optimization Studies

Although we believe that the desorption of picric acid from Porapak R could be improved with further optimization studies, time and monies did not allow additional work in this area. Therefore, precision and accuracy testing were performed using methanol containing 0.05M tetrabutyl ammonium hydroxide as the eluant.

Table 32. Screening Studies with Picric Acid *

Sorbent	Concentration of Picric Acid in Filtrate	% Leakage
XAD-4	89.9 µg/L	8.6
XAD-7	219.8 µg/L	21.1
XE-340	380 µg/L	36.5
XE-348	ND**	ND
Porapak R	10.2 µg/L	1.0
Porapak S	6.50 µg/L	6.5

*Water was analyzed without extraction by HPLC using a reverse phase C-18 radial compression column; carrier solvent consists of 50% acetonitrile, 50% water, made to 0.005M with tetrabutylammonium hydroxide buffered to 6.5 with H_3PO_4 at 2.0 mL/min; UV detection at 205 nm (lower detection limit is less than 25 µg/L - four-day precision and accuracy not performed).

**ND - none detected.

IV. PRECISION AND ACCURACY TESTING OF SOLID SORBENT METHODS

A. TNT, 2,4-DNT, 2,6-DNT and RDX on Porapak S

The method tested is described in detail in Appendix C. Basically, the sorbent (Porapak S) was pre-washed with acetone by two hours treatment in a soxhlet extractor. After drying in a vacuum oven at 30°C for one hour, approximately 3 mL of the sorbent was packed into graduated disposable 5 mL pipets and retained with wads of glass wool. At this point, the sorbent tubes were washed and conditioned by pumping 50 mL of acetone and 50 mL of water through each tube.

For precision and accuracy testing, a stock solution was prepared in 69% aqueous methanol which contained 0.804, 0.901, 1.002 and 0.951 mg/L of RDX, TNT, 2,4-DNT and 2,6-DNT, respectively. Spiked samples for precision and accuracy testing were prepared by adding 0.0, 0.5, 1.0, 2.0, 5.0 and 10.0 mL of the stock solution to a 1 liter volumetric and bringing up to volume with standard water. This series of samples was tested daily for four days.

Sampling was accomplished by pumping each one liter solution through a conditioned sorbent tube. The loaded tubes were blown dry for several minutes with nitrogen and placed in the reverse desorption apparatus. Desorption was accomplished by adding 10 mL of acetone (in two 5 mL portions) to the upper glass tube of the assembly. Pressure was then applied with an autopipet bulb until the acetone began dripping from the tube. The tube was then allowed to flow slowly on its own for 5 to 10 minutes at which point pressure was applied to lower the acetone level so that the second 5 mL portion of acetone could be added. After an additional 5 to 10 minutes of gravity flow, manual pressure was applied to force the remaining acetone from the tube. A measured 7.5 mL of acetone was collected. For GC analysis, 1 mL of the acetone eluate was diluted to 5 mL with benzene and dried over anhydrous sodium sulfate. For HPLC analysis, 2 mL of the acetone sample were blown dry with nitrogen and redissolved in 2 mL of methylene chloride.

Gas chromatographic analysis was performed for TNT and the isomeric DNT's on a Hewlett-Packard 5880 computer controlled gas chromatograph equipped with an autoinjector and an electron capture detector. The following conditions were employed:

Column:	6 ft. x 0.25 in. I.D. glass column packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 supelcoport	
Temperatures:	injection port	210°C
	oven	185°C
	detector	300°C

Carrier Nitrogen @ 28 cc/min

Retention Time:	2,6-DNT	1.3 min.
	2,4-DNT	1.7 min.
	TNT	3.2 min.

HPLC analysis of RDX was performed on a Perkin-Elmer model 601 HPLC equipped with a model LC-55 variable wavelength visible/UV detector and a Waters Radial Compression column system. The conditions employed are:

Column:	10 cm x 7 mm radical compression column packed with 10 micron normal phase silica
Mobile Phase:	61% Hexane, 26% Methylene Chloride, 13% Acetonitrile
Flow Rate:	1.5 mL/min
Detector:	UV @ 232 nm

The concentrations of TNT, 2,4-DNT and 2,6-DNT in the original water were calculated according to the following formula:

$$\text{Found Concentration} = (\text{analyzed concentration}) \times \frac{(\text{extract volume})}{1 \text{ liter (water)}} \times 5.$$

The RDX concentration in the original water was calculated by the formula:

$$\text{Found Concentration} = (\text{analyzed concentration}) \times \frac{(\text{extract volume})}{1 \text{ liter}} .$$

The found and target values for the four-day study were input into the Atlantic Research Corporation version of the USATHAMA detection limit computer program. A summary of the data and the program outputs are shown in Tables 33 through 39. The standard deviation, percent inaccuracy and percent imprecision are plotted in Figures 7 through 14. Correlation coefficients in excess of 0.99 were obtained for all but RDX and were obtained for RDX when the high (10 DL) level was omitted from the statistics. Detection limits of 1.50, 1.53, 0.97 and 1.69 µg/L were obtained for TNT, RDX, 2,6-DNT, and 2,4-DNT, respectively, when all data (0-10 DL) was employed. Lower detection limits were obtained when the high level (10 DL) was omitted from the statistics.

In summary, the solid sorbents method using Porapak S for concentration of TNT, 2,4-DNT, 2,6-DNT and RDX from water appears to be a reliable method for analysis. Detection limits for all of the explosives are less than 2 µg/L. The detection limits for TNT, 2,4-DNT, and 2,6-DNT could easily be improved by a factor of 5 if the acetone were blown dry and the explosives reconstituted in benzene. The RDX detection limit could be lowered by concentration of the eluate (e.g. blow dry of 4 mL and reconstituted to 1 mL with methylene chloride). Recoveries for all explosives were nearly quantitative, i.e. TNT - 92.55%; 2,4-DNT - 84.69%; 2,6-DNT - 100.88%; and RDX - 99.2%; with 2,4-DNT having the lowest recovery of approximately 85%.

Table 33. Detection Limit Calculations for TNT via Solid Sorbent Tube Sampling

USATHAMA DETECTION LIMIT PROGRAM

SUM(Y(I))= 66.8500
SUM(X(I))= 66.6800
SUM(X(I)↑2)= 423.0908
SUM(Y(I)↑2)= 393.3205
SUM(X(I)*Y(I))= 405.8520
X= 1.0805 Y + -0.2312 CORR. COEF.= 0.9911
Y= 0.9255 X + 0.2140 CORR. COEF.= 0.9911

LINE	TC	C(FOUND)	C(CALC)	DELTA	IFLAG
1	0.0000	0.0800	0.2140	-0.1340	0.0000
2	0.0000	0.6800	0.2140	0.4660	0.0000
3	0.0000	0.0100	0.2140	-0.2040	0.0000
4	0.0000	0.1000	0.2140	-0.1140	0.0000
5	0.4500	0.5900	0.6305	-0.0405	1.0000
6	0.4500	0.4100	0.6305	-0.2205	1.0000
7	0.4500	0.6000	0.6305	-0.0305	1.0000
8	0.4500	0.6600	0.6305	0.0295	1.0000
9	0.9000	0.9400	1.0470	-0.1070	1.0000
10	0.9000	0.9900	1.0470	-0.0570	1.0000
11	0.9000	1.0200	1.0470	-0.0270	1.0000
12	0.9000	1.1100	1.0470	0.0630	1.0000
13	1.8000	1.3800	1.8799	-0.4999	1.0000
14	1.8000	1.5700	1.8799	-0.3099	1.0000
15	1.8000	1.8100	1.8799	-0.0699	1.0000
16	1.8000	2.1000	1.8799	0.2201	1.0000
17	4.5100	4.3300	4.3881	-0.0581	4.0000
18	4.5100	4.1300	4.3881	-0.2581	4.0000
19	4.5100	5.2100	4.3881	0.8219	4.0000
20	4.5100	5.6400	4.3881	1.2519	4.0000
21	9.0100	8.0500	8.5530	-0.5030	5.0000
22	9.0100	8.4800	8.5530	-0.0730	5.0000
23	9.0100	8.3300	8.5530	-0.2230	5.0000
24	9.0100	8.6300	8.5530	0.0770	5.0000

STANDARD ERROR OF ESTIMATE (Sxy) = 0.1914
N= 24.0000 n= 1.0000
TOTAL N= 24.0000
t= 1.7170
t BASED ON TOTAL N
UPPER CONFIDENCE LIMIT AT(X=0) = 0.9133

upper confidence line at X= 0.4500 is 1.1256
lower confidence line at X= 0.4500 is -0.0644
STANDARD DEVIATION AT X= 0.4500 is 0.1079
PERCENT INACCURACY AT X= 0.4500 IS 25.5556
PERCENT IMPRECISION AT X= 0.4500 IS 19.0899
MEAN FOUND AT X= 0.4500 IS 0.5650

upper confidence line at X= 0.9000 is 1.7394
lower confidence line at X= 0.9000 is 0.1545
STANDARD DEVIATION AT X= 0.9000 is 0.0714
PERCENT INACCURACY AT X= 0.9000 IS 12.7778
PERCENT IMPRECISION AT X= 0.9000 IS 7.0359
MEAN FOUND AT X= 0.9000 IS 1.0150

upper confidence line at X= 1.8000 is 1.5669
lower confidence line at X= 1.8000 is 1.1910
STANDARD DEVIATION AT X= 1.8000 is 0.0912
PERCENT INACCURACY AT X= 1.8000 IS -4.1722
PERCENT IMPRECISION AT X= 1.8000 IS 13.1446
MEAN FOUND AT X= 1.8000 IS 1.7150

upper confidence line at X= 4.5100 is 5.0739
lower confidence line at X= 4.5100 is 3.6954
STANDARD DEVIATION AT X= 4.5100 is 0.7166
PERCENT INACCURACY AT X= 4.5100 IS 7.0399
PERCENT IMPRECISION AT X= 4.5100 IS 14.5418
MEAN FOUND AT X= 4.5100 IS 4.3847

upper confidence line at X= 9.0100 is 9.3922
lower confidence line at X= 9.0100 is 7.8135
STANDARD DEVIATION AT X= 9.0100 is 0.2474
PERCENT INACCURACY AT X= 9.0100 IS -5.0755
PERCENT IMPRECISION AT X= 9.0100 IS 2.9554
MEAN FOUND AT X= 9.0100 IS 8.6028

DETECTION LIMIT = 1.4993 µg/mL

Table 34. Detection Limit Data Summary for TNT

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	.08	.68	.01	.10	.22	.31	140.9	
.45	.59	.41	.60	.66	.57	.11	19.9	25.6
.90	.94	.99	1.02	1.11	1.02	.07	7.0	12.8
1.80	1.38	1.57	1.81	2.10	1.72	.31	18.1	-4.7
4.51	4.33	4.13	5.21	5.64	4.83	.72	14.8	7.0
5.01	8.05	8.48	8.33	8.63	8.37	.25	3.0	-7.1

Y = 0.9235X + 0.2140

Correlation Coefficient = 0.9918

Detection Limit = 1.50 µg/L

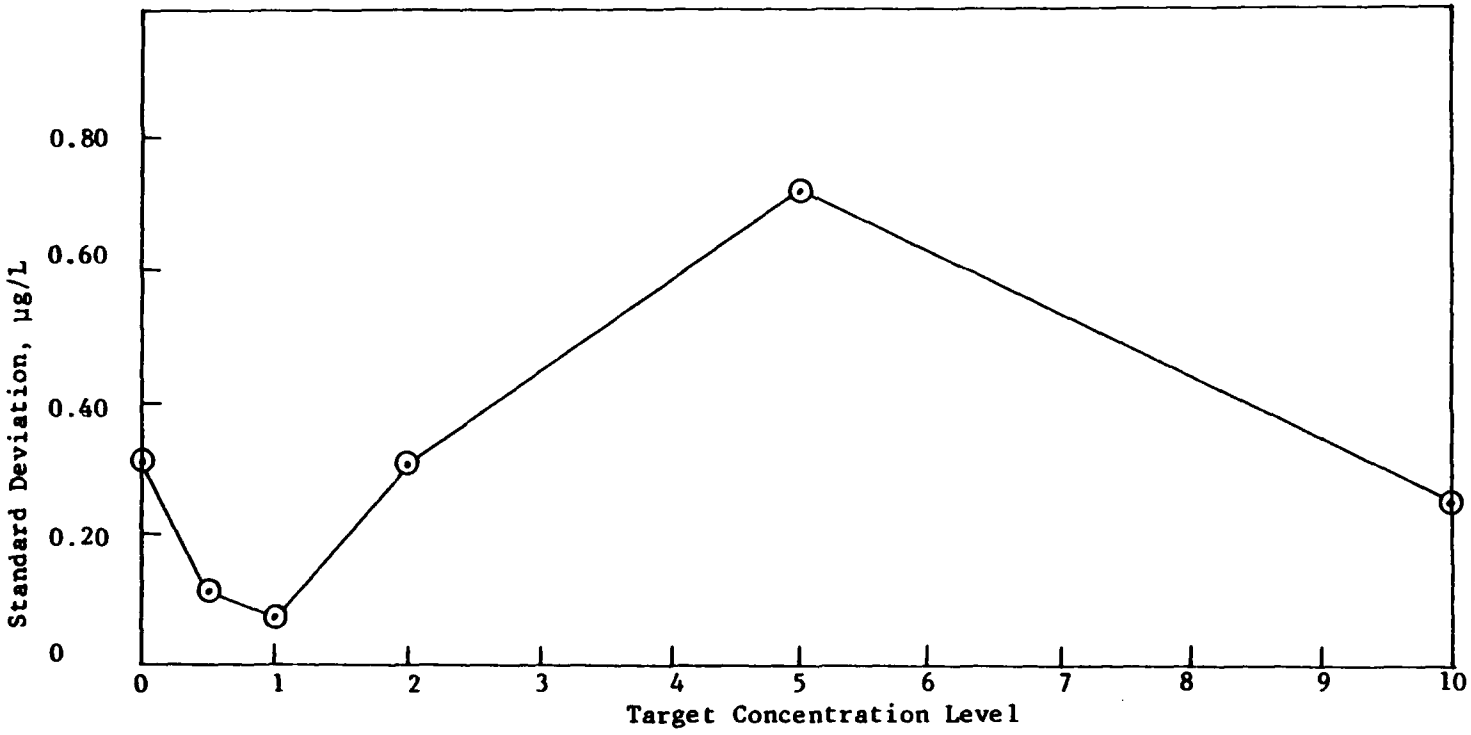


Figure 7. Standard Deviation - TNT Solid Sorbent Tube Sampling

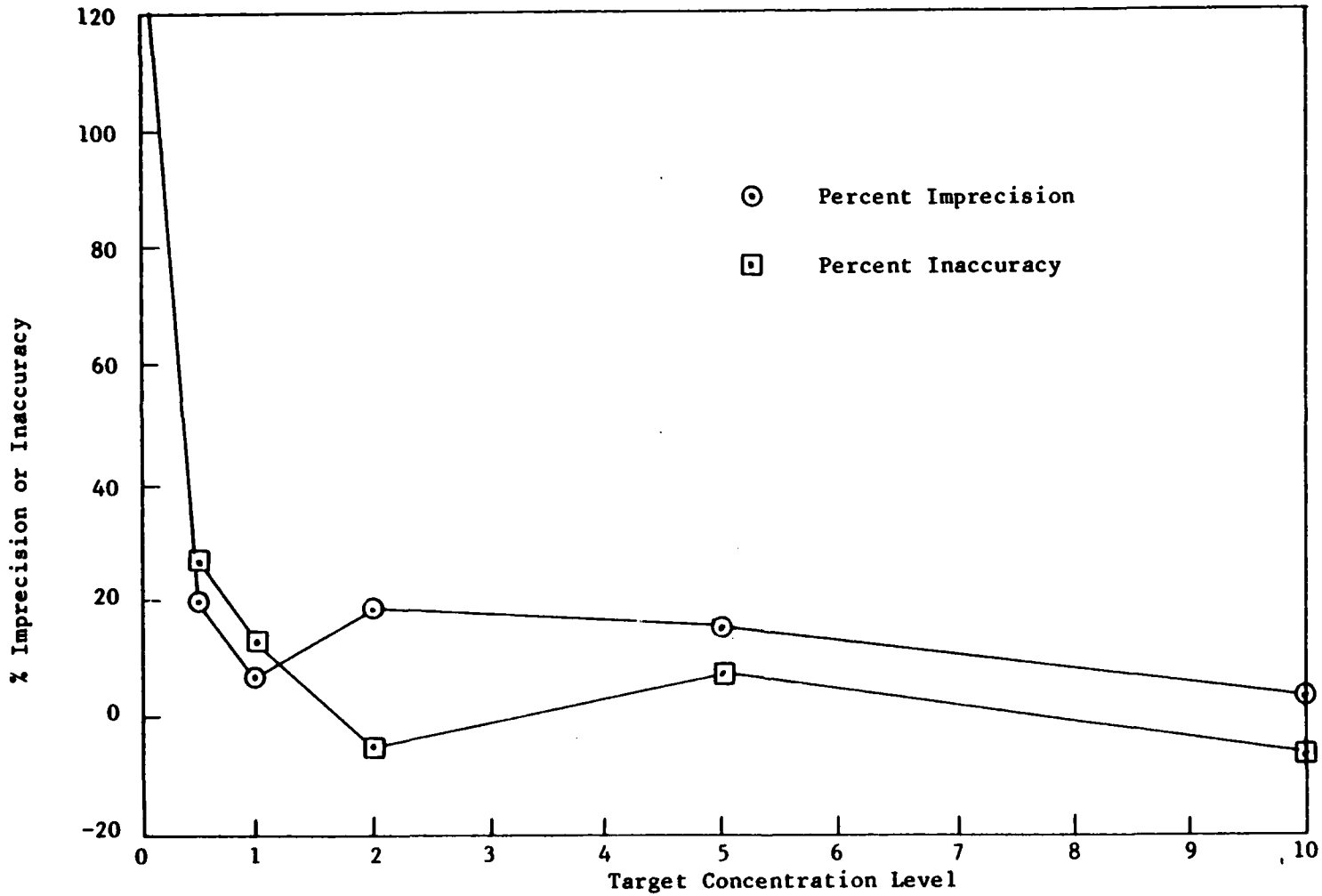


Figure 8. Percent Imprecision and Percent Inaccuracy - TNT Solid Sorbent Tube Sampling

Table 35. Detection Limit Calculations for 2,4-DNT via Solid Sorbent Tube Sampling

```
USATHAMA DETECTION LIMIT PROGRAM


SUM(X(i))=              73.6960
SUM(C(i))=              74.1200
SUM(X(i)^2)=             523.0020
SUM(C(i)^2)=             440.8379
SUM(C(i)*Y(i))=          476.6665
X=          1.1305 Y +   -0.5374     CORR. COEF.=  0.9[illegible]
Y=          0.8469 X +    0.4552     CORR. COEF.=  0.9[illegible]

LINE      TC       C(FOUND)    C(CALC)      DELTA        [illegible]
  1      0.0000      0.2600      0.4552     -0.1952      [illegible]
  2      0.0000      0.1700      0.4552     -0.2852      [illegible]
  3      0.0000      0.3200      0.4552     -0.1352      [illegible]
  4      0.0000      0.4000      0.4552     -0.0552      [illegible]
  5      0.5000      0.8500      0.8786     -0.0286      [illegible]
  6      0.5000      0.6000      0.8786     -0.2786      [illegible]
  7      0.5000      0.8200      0.8786     -0.0586      [illegible]
  8      0.5000      0.9300      0.8786      0.0514      [illegible]
  9      1.0000      1.2800      1.3021     -0.0221      [illegible]
 10      1.0000      1.2900      1.3021     -0.0121      [illegible]
 11      1.0000      1.2000      1.3021     -0.1021      [illegible]
 12      1.0000      1.4700      1.3021      0.1679      [illegible]
 13      2.0000      1.9600      2.1490     -0.1890      [illegible]
 14      2.0000      1.9660      2.1490     -0.1830      [illegible]
 15      2.0000      2.0400      2.1490     -0.1090      [illegible]
 16      2.0000      2.3700      2.1490      0.2210      [illegible]
 17      5.0100      5.1100      4.6981      0.4119      [illegible]
 18      5.0100      4.3800      4.6981     -0.3181      [illegible]
 19      5.0100      5.5700      4.6981      0.8719      [illegible]
 20      5.0100      6.0300      4.6981      1.3319      [illegible]
 21     10.0200      8.5400      8.9411     -0.4011      [illegible]
 22     10.0200      8.6500      8.9411     -0.2911      [illegible]
 23     10.0200      8.5400      8.9411     -0.4011      [illegible]
 24     10.0200      8.9500      8.9411      0.0089      [illegible]
.....................................
STANDARD  ERROR OF ESTIMATE (Sx) =              0.[illegible]
N=          24.0000   n=              1.0000
TOTAL N=            24.0000
t=              1.7170
t BASED ON TOTAL N
UPPER CONFIDENCE LIMIT AT(X=0) =              1.1[illegible]


upper confidence line at X=              0.5000 is              [illegible]
lower confidence line at X=              0.5000 is              [illegible]
STANDARD DEVIATION AT X=                 0.5000  is              [illegible]
PERCENT INACCURACY AT X=                 0.5000  IS            [illegible]
PERCENT IMPRECISION AT X=                0.5000  IS            [illegible]
MEAN FOUND AT  X=              0.5000  IS                [illegible]

upper confidence line at X=              1.0000 is              [illegible]
lower confidence line at X=              1.0000 is              [illegible]
STANDARD DEVIATION AT X=                 1.0000  is              [illegible]
PERCENT INACCURACY AT X=                 1.0000  IS            [illegible]
PERCENT IMPRECISION AT X=                1.0000  IS            [illegible]
MEAN FOUND AT  X=              1.0000  IS                [illegible]

upper confidence line at X=              2.0000 is              [illegible]
lower confidence line at X=              2.0000 is              [illegible]
STANDARD DEVIATION AT X=                 2.0000  is              [illegible]
PERCENT INACCURACY AT X=                 2.0000  IS            [illegible]
PERCENT IMPRECISION AT X=                2.0000  IS            [illegible]
MEAN FOUND AT  X=              2.0000  IS                [illegible]

upper confidence line at X=              5.0100 is              [illegible]
lower confidence line at X=              5.0100 is              [illegible]
STANDARD DEVIATION AT X=                 5.0100  is              [illegible]
PERCENT INACCURACY AT X=                 5.0100  IS            [illegible]
PERCENT IMPRECISION AT X=                5.0100  IS            [illegible]
MEAN FOUND AT  X=              5.0100  IS                [illegible]

upper confidence line at X=             10.0200 is              [illegible]
lower confidence line at X=             10.0200 is              [illegible]
STANDARD DEVIATION AT X=                10.0200  is              [illegible]
PERCENT INACCURACY AT X=                10.0200  IS            [illegible]
PERCENT IMPRECISION AT X=               10.0200  IS            [illegible]
MEAN FOUND AT  X=             10.0200  IS                [illegible]

|-----------------------------------------|
|  DETECTION LIMIT  =            1.6910   | µg/L
|-----------------------------------------|
```

Table 36. Detection Limit Data Summary for 2,4-DNT

Target Concentration	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
(µg/L)								
0	.26	.17	.32	.40	.29	.097	33.8	
0.5	.85	.60	.82	.93	.80	.14	17.6	60.0
1.0	1.28	1.29	1.20	1.47	1.31	.11	8.7	31.0
2.0	1.96	1.96	2.04	2.37	2.08	.20	9.4	4.1
5.01	5.11	4.38	5.57	6.03	5.27	.70	13.3	5.2
10.02	8.53	8.65	8.54	8.95	8.67	.19	2.2	-13.5

$Y = 0.8469X + 0.4552$

Correlation Coefficient = 0.9916

Detection Limit = 1.69 µg/L

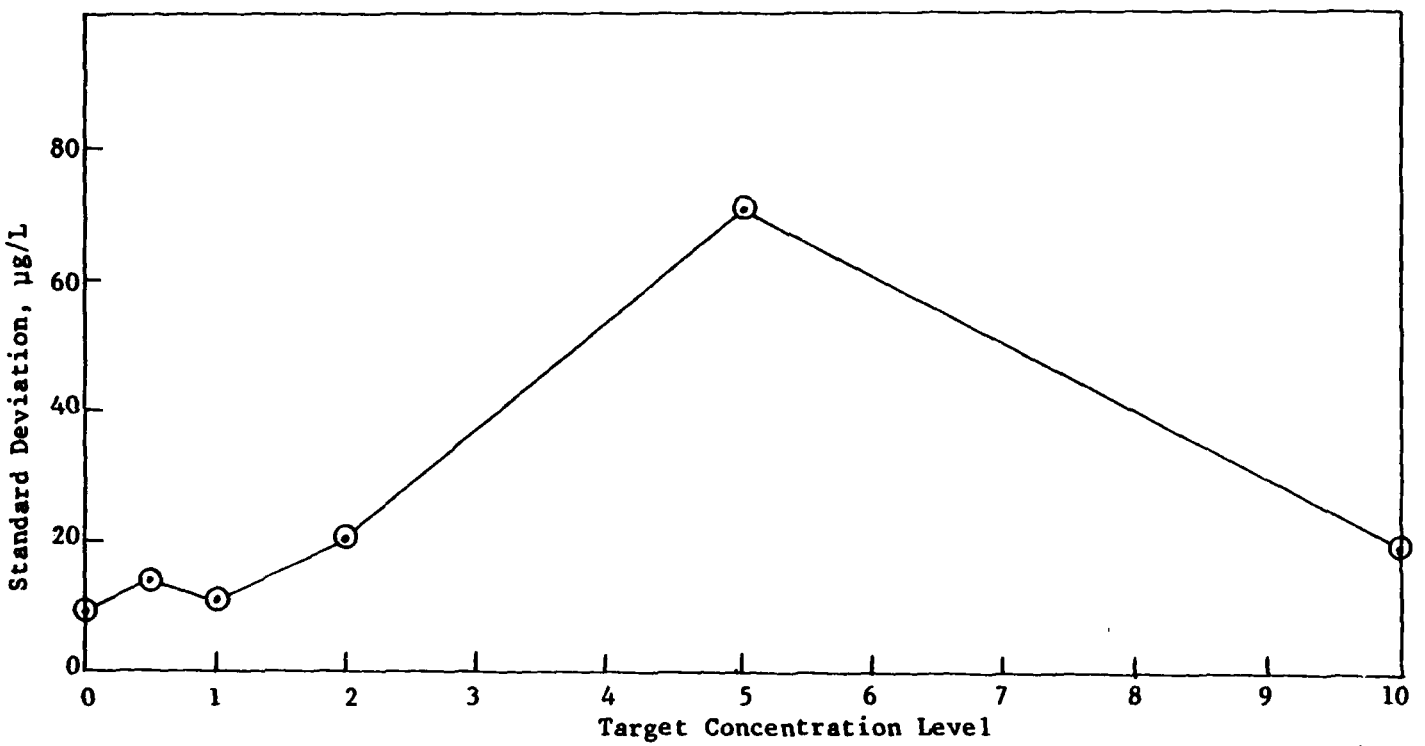


Figure 9. Standard Deviation - 2,4-DNT Solid Sorbent Tube Sampling

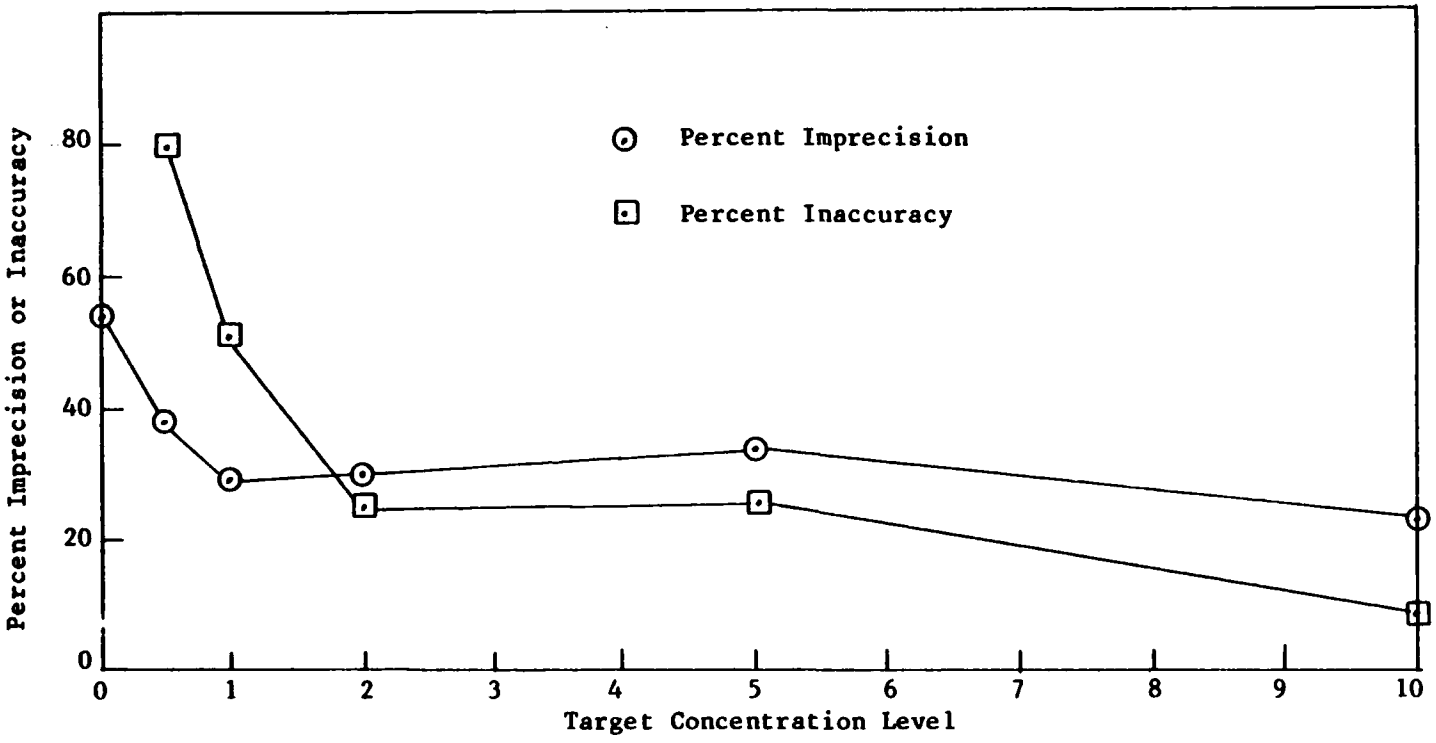


Figure 10. Percent Imprecision and Percent Inaccuracy - 2,4-DNT Solid Sorbent Tube Sampling

Table 37. Detection Limit Calculations for 2,6-DNT via Solid Sorbent Tube Sampling

```
PSUM(Y(i))=            75.8800
SUM(X(i))=             70.4900
SUM(X(i))↑2=           471.7125
SUM(Y(i))↑2=           510.9208
SUM(X(i)*Y(i))=        489.8635
X=        0.9913 Y +  -0.1971    CORR. COEF.=  0.9969
Y=        1.0088 X +   0.1988    CORR. COEF.=  0.9969

LINE      TC      C(FOUND)    C(CALC)      DELTA        GROUP
  1      0.0000     0.2100     0.1988      0.0112      0.0000
  2      0.0000     0.1600     0.1988     -0.0388      0.0000
  3      0.0000     0.0000     0.1988     -0.1988      0.0000
  4      0.0000     0.0000     0.1988     -0.1988      0.0000
  5      0.4800     0.8100     0.6830      0.1270      1.0000
  6      0.4800     0.5900     0.6830     -0.0930      1.0000
  7      0.4800     0.7400     0.6830      0.0570      1.0000
  8      0.4800     0.7900     0.6830      0.1070      1.0000
  9      0.9500     1.2300     1.1572      0.0728      1.0000
 10      0.9500     1.2900     1.1572      0.1328      2.0000
 11      0.9500     1.1600     1.1572      0.0028      2.0000
 12      0.9500     1.3000     1.1572      0.1428      2.0000
 13      1.9000     1.9900     2.1155     -0.1255      3.0000
 14      1.9000     1.9700     2.1155     -0.1455      3.0000
 15      1.9000     2.1400     2.1155      0.0245      3.0000
 16      1.9900     2.3500     2.2063      0.1437      3.0000
 17      4.7600     4.8300     5.0006     -0.1706      4.0000
 18      4.7600     4.1400     5.0006     -0.8606      4.0000
 19      4.7600     5.3800     5.0006      0.3794      4.0000
 20      4.7600     5.6800     5.0006      0.6794      4.0000
 21      9.5100     9.7600     9.7922     -0.0322      5.0000
 22      9.5100     9.5900     9.7922     -0.2022      5.0000
 23      9.5100     9.7900     9.7922     -0.0022      5.0000
 24      9.5100     9.9900     9.7922      0.1978      5.0000
.....
STANDARD  ERROR OF ESTIMATE (Sxy) =              0.1760
N=          24.0000   n=            1.0000
TOTAL N=              24.0000
t=            1.7170
t BASED ON TOTAL N
UPPER CONFIDENCE LIMIT AT(X=0) =              0.5899


upper confidence line at X=            0.4800 is              1.1719
lower confidence line at X=            0.4800 is              0.1941
STANDARD DEVIATION AT X=               0.4800  is             0.0635
PERCENT INACCURACY AT X=             0.4800  IS            51.6041
PERCENT IMPRECISION AT X=            0.4800  IS            13.2***
MEAN FOUND AT  X=          0.4800  IS              0.7***

upper confidence line at X=            0.9500 is              1.6442
lower confidence line at X=            0.9500 is              0.6701
STANDARD DEVIATION AT X=               0.9500  is             0.0624
PERCENT INACCURACY AT X=             0.9500  IS            30.7***
PERCENT IMPRECISION AT X=            0.9500  IS             5.3208
MEAN FOUND AT  X=          0.9500  IS              1.2***

upper confidence line at X=            1.9900 is              2.6307
lower confidence line at X=            1.9900 is              1.7219
STANDARD DEVIATION AT X=               1.9900  is             0.1756
PERCENT INACCURACY AT X=             1.9900  IS             6.15**
PERCENT IMPRECISION AT X=            1.9900  IS             8.3110
MEAN FOUND AT  X=          1.9900  IS              2.1***

upper confidence line at X=            4.7600 is              5.4371
lower confidence line at X=            4.7600 is              4.5141
STANDARD DEVIATION AT X=               4.7600  is             0.***0
PERCENT INACCURACY AT X=             4.7600  IS             5.1***
PERCENT IMPRECISION AT X=            4.7600  IS            11.5201
MEAN FOUND AT  X=          4.7600  IS              5.00**

upper confidence line at X=            9.5100 is             10.3123
lower confidence line at X=            9.5100 is              9.2***
STANDARD DEVIATION AT X=               9.5100  is             0.1640
PERCENT INACCURACY AT X=             9.5100  IS             1.6***
PERCENT IMPRECISION AT X=            9.5100  IS             1.7***
MEAN FOUND AT  X=          9.5100  IS              9.7***

|-----------------------------------------|
|  DETECTION LIMIT  =            0.9696 ppm |
|-----------------------------------------|
```

Table 38. Detection Limit Data Summary for 2,6-DNT

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	.21	.16	.0	.0	.09	.11	117.6	
.48	.81	.59	.74	.79	.73	.10	13.6	52.6
.95	1.23	1.28	1.16	1.30	1.24	.06	5.0	30.8
1.90	1.99	1.97	2.18	2.35	2.11	.18	8.3	11.2
4.76	4.83	4.14	5.38	5.68	5.01	.68	13.5	5.2
9.51	9.76	9.59	9.79	9.99	9.78	.16	1.6	2.9

Y = 1.0088X + 0.1988

Correlation Coefficient = .9969

Detection Limit = 0.97 µg/L

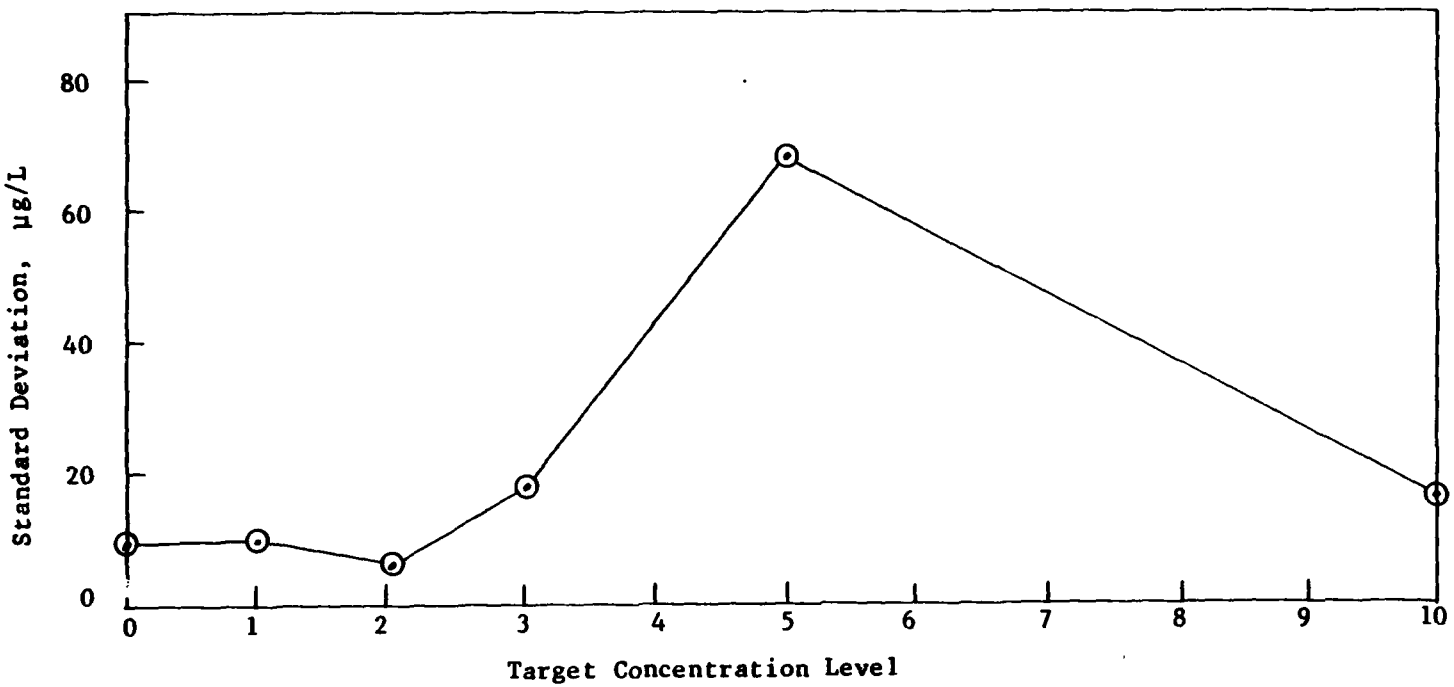


Figure 11. Standard Deviation - 2,6-DNT Solid Sorbent Tube Sampling

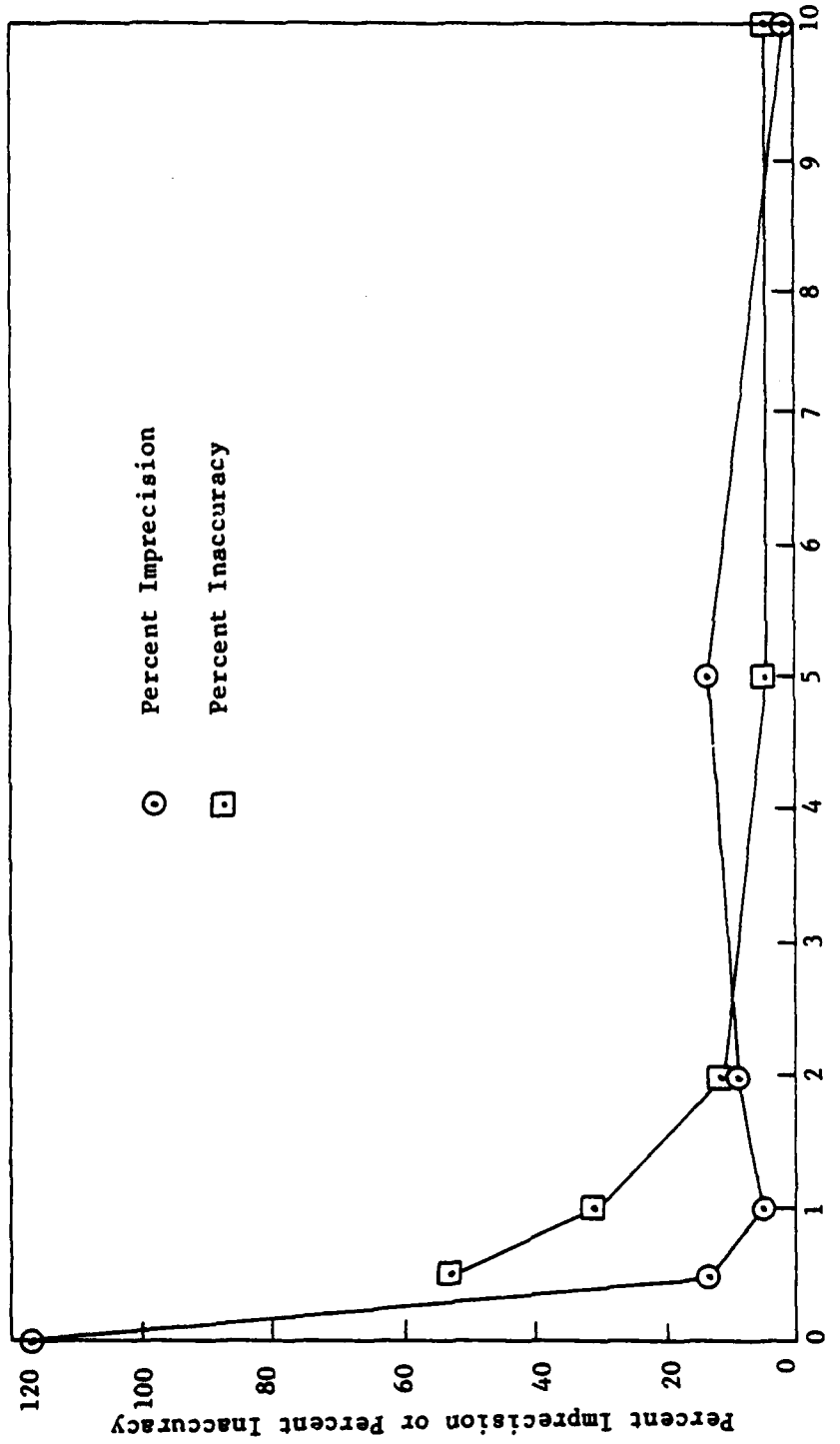


Figure 12. Percent Imprecision and Percent Inaccuracy - 2,6-DNT Solid Sorbent Tube Sampling

Table 39. Detection Limit Calculations for RDX via Solid Sorbent Tube Sampling

```
SUM(Y(i))=              16.7800
SUM(X(i))=              27.3340
SUM(X(i))^2=              78.2131
SUM(Y(i))^2=              76.6398
SUM(X(i)*Y(i))=              77.1342
X=          1.0079 Y +    0.0171     CORR. COEF.=   0.9910
Y=          0.9921 X +   -0.0169     CORR. COEF.=   0.9910

LINE      TC      C(FOUND)    C(CALC)      DELTA        GROUP
  1      0.0000     0.0000     -0.0169      0.0169      1.0000
  2      0.0000     0.0000     -0.0169      0.0169      1.0000
  3      0.0000     0.0000     -0.0169      0.0169      1.0000
  4      0.0000     0.0000     -0.0169      0.0169      1.0000
  5      0.4020     0.4200      0.3819      0.0381      1.0000
  6      0.4020     0.3100      0.3819     -0.0719      1.0000
  7      0.4020     0.2500      0.3819     -0.1319      1.0000
  8      0.4020     0.3400      0.3819     -0.0419      1.0000
  9      0.8040     0.8300      0.7807      0.0493      2.0000
 10      0.8020     0.7900      0.7787      0.0113      2.0000
 11      0.8040     0.6600      0.7807     -0.1207      2.0000
 12      0.8040     0.7000      0.7807     -0.0807      2.0000
 13      1.6080     1.5100      1.5784     -0.0684      3.0000
 14      1.6080     1.8600      1.5784      0.2816      3.0000
 15      1.6080     1.4900      1.5784     -0.0884      3.0000
 16      1.6080     1.8400      1.5784      0.2616      3.0000
 17      4.0200     3.6100      3.9714     -0.3614      4.0000
 18      4.0200     3.7900      3.9714     -0.1814      4.0000
 19      4.0200     3.9700      3.9714     -0.0014      4.0000
 20      4.0200     4.4100      3.9714      0.4386      4.0000
.....
STANDARD  ERROR OF ESTIMATE (Sxy) =              0.1774
N=          20.0000   n=              1.0000
TOTAL N=            20.0000
t=            1.7340
t BASED ON TOTAL N
UPPER CONFIDENCE LIMIT AT(X=0) =              0.3051


upper confidence line at X=              0.4020 is              0.7306
lower confidence line at X=              0.4020 is              0.3632
STANDARD DEVIATION AT X=              0.4020  is              0.0707
PERCENT INACCURACY AT X=              0.4020  IS             -17.9104
PERCENT IMPRECISION AT X=             0.4020  IS              31.4279
MEAN FOUND AT  X=          0.4020  IS              0.5300

upper confidence line at X=              0.8040 is              1.0972
lower confidence line at X=              0.8040 is              0.4641
STANDARD DEVIATION AT X=              0.8040  is              0.0785
PERCENT INACCURACY AT X=              0.8040  IS             -7.3383
PERCENT IMPRECISION AT X=             0.8040  IS              10.5407
MEAN FOUND AT  X=          0.8040  IS              0.7450

upper confidence line at X=              1.6080 is              1.9909
lower confidence line at X=              1.6080 is              1.2429
STANDARD DEVIATION AT X=              1.6080  is              0.1024
PERCENT INACCURACY AT X=              1.6080  IS              4.1667
PERCENT IMPRECISION AT X=             1.6080  IS              12.0837
MEAN FOUND AT  X=          1.6080  IS              1.6750

upper confidence line at X=              4.0200 is              4.3116
lower confidence line at X=              4.0200 is              3.6312
STANDARD DEVIATION AT X=              4.0200  is              0.3411
PERCENT INACCURACY AT X=              4.0200  IS             -1.3657
PERCENT IMPRECISION AT X=             4.0200  IS              8.6964
MEAN FOUND AT  X=          4.0200  IS              3.9450

|-----------------------------------------|
|  DETECTION LIMIT  =            0.6443   |
|-----------------------------------------|
```

Table 40. Detection Limit Data Summary for RDX

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	.0	.0	.0	.0	.0			
.402	.42	.31	.25	.34	.33	.07	21.4	-17.9
.804	.83	.79	.66	.70	.73	.10	14.0	- 9.2
1.608	1.51	1.86	1.49	1.84	1.68	.20	12.1	4.2
4.02	3.61	3.79	3.97	4.41	3.95	.34	8.7	- 1.9
8.04	6.35	6.54	6.02	6.90	6.45	.37	5.7	-19.7

Y = 0.816X + 0.107; detection limit = 1.53 µg/L; Correlation Coefficient = 0.9897 (all data 0-10 DL)

Y = 0.992X - 0.0169; detection limit = 0.64 µg/L; Correlation Coefficient = 0.9930 (0-5 DL) data only)

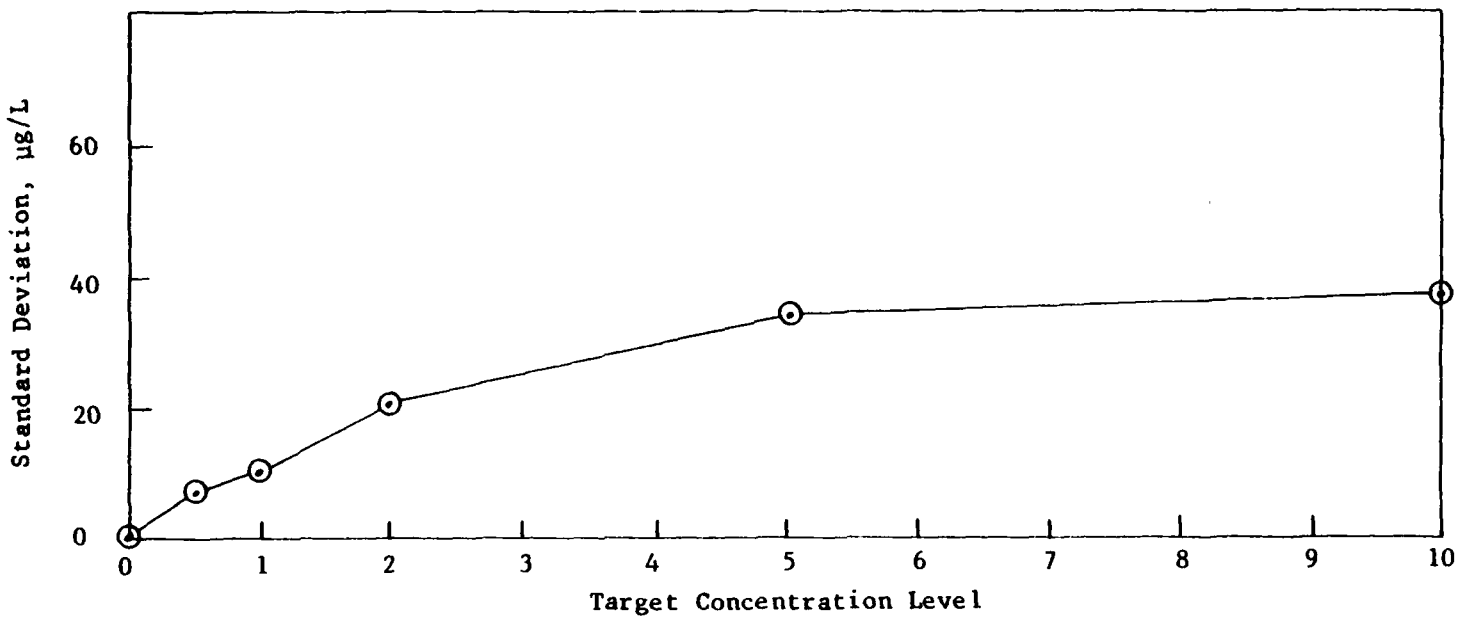
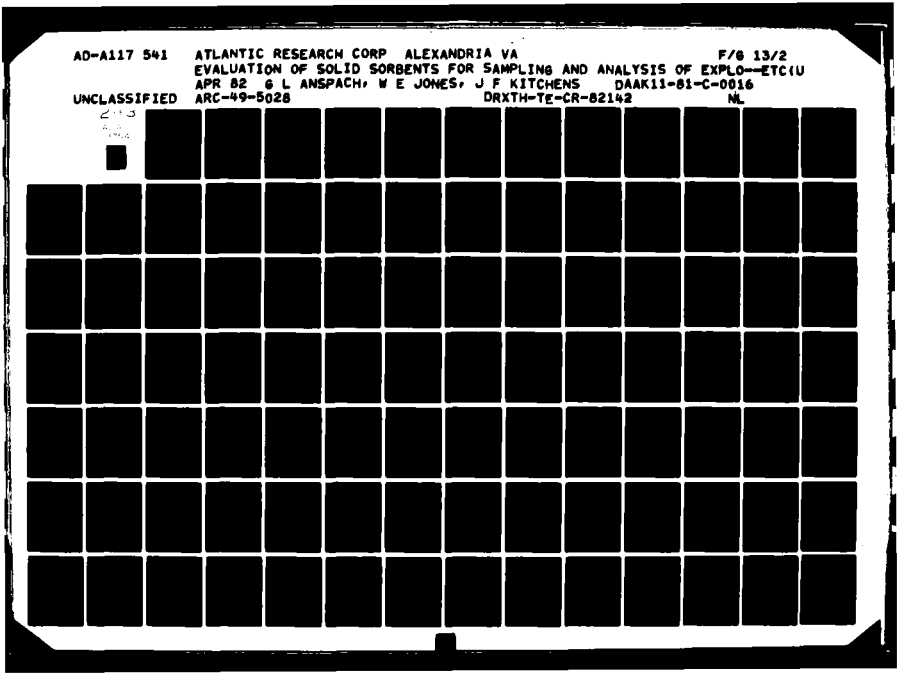
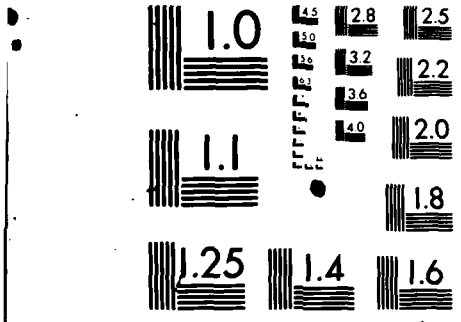


Figure 13. Standard Deviation - RDX Solid Sorbent Tube Sampling

AD-A117 541 ATLANTIC RESEARCH CORP ALEXANDRIA VA F/G 13/2
EVALUATION OF SOLID SORBENTS FOR SAMPLING AND ANALYSIS OF EXPLO--ETC(U
APR 82 G L ANSPACH, W E JONES, J F KITCHENS DAAK11-81-C-0016
UNCLASSIFIED ARC-49-5028 DRXTH-TE-CR-82142 NL





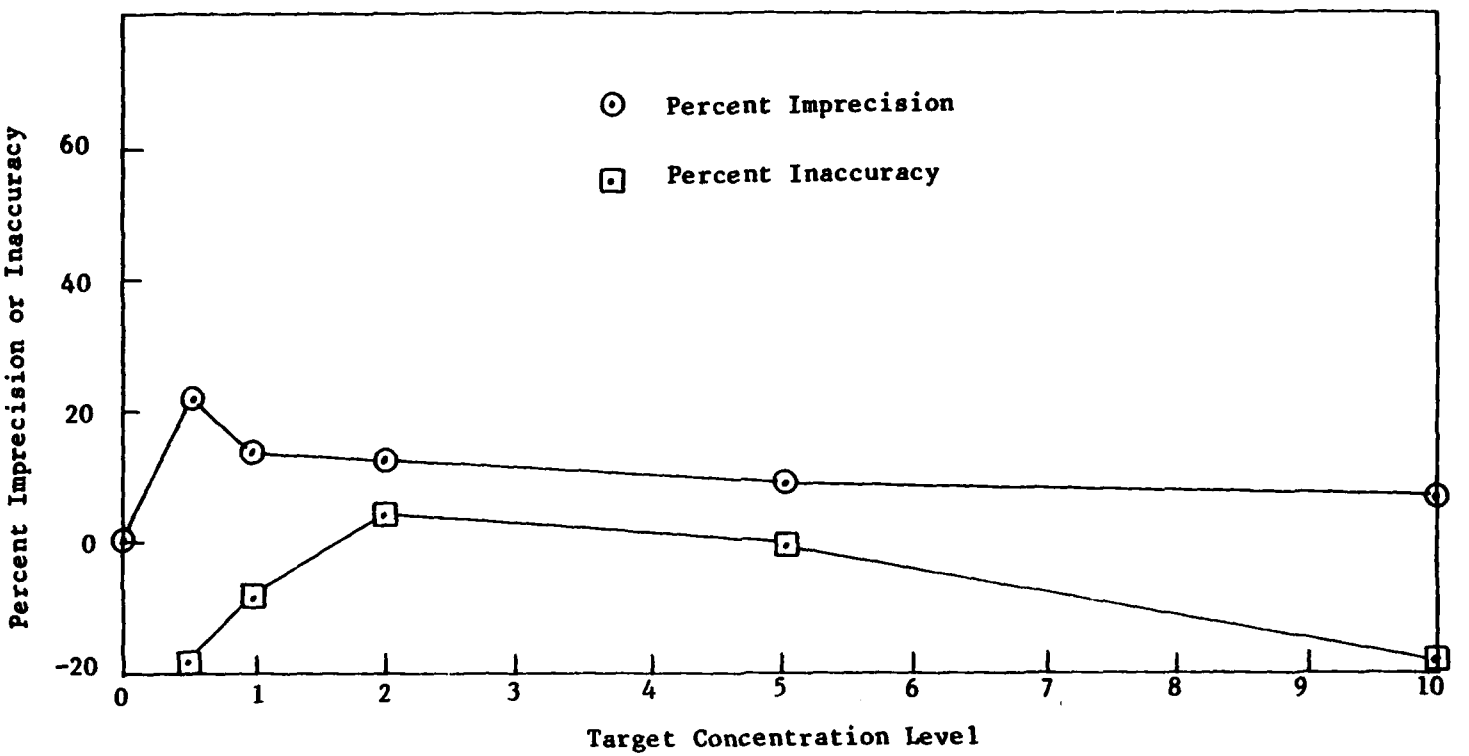


Figure 14. Percent Imprecision and Percent Inaccuracy - RDX Solid Sorbent Tube Sampling

B. Tetryl on XAD-4

The method tested for tetryl is described in detail in Appendix C. The XAD-4 sorbent was pre-washed by soxhlet extraction with acetone for two hours. The packed sorbent tubes were then conditioned by pumping 50 mL of acetone and 50 mL of distilled water through each tube.

A stock solution of 1.478 mg/L of tetryl was prepared by diluting 5 mL of a 295.6 mg/L benzene solution to 1 liter with 55% aqueous methanol. Spiked samples were then prepared by diluting 0.0, 0.5, 1.0, 2.0, 5.0 and 10.0 mL of this stock to 1 liter with standard water yielding samples which are 0, 0.74, 1.48, 7.39, and 14.78 µg/L. One each of these spiked samples was sampled and analyzed on each of four successive days.

Desorption of the loaded tubes was performed in the following manner. The tubes were dried for 2 to 3 minutes with a stream of nitrogen and inverted in the reverse desorption apparatus. ONe mL of methanol was forced through the tube. Then 10 mL benzene was allowed to gravity drain through the sorbent. Five to seven mL of the eluate were collected and centrifuged. The upper benzene layer was removed with a 5 mL pipet and measured. Analysis of the benzene layer was performed on a Varian 3700 gas chromatograph equipped with an electron capture detector and a model 8000 autosampler. The following conditions were employed:

Column:	6 ft. x 0.25 in. glass column packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 supelcoport	
Temperature:	injection port	210°C
	oven	200°C
	detector	300°C

Carrier Nitrogen @ 28 cc/min.

Injector Volume: 2 µL

Retention Time: 4.5 min.

Eluate concentrations were calculated by interpolation between appropriate standards (due to the non-linearity of the standard curve, a greater than normal number of standards was employed). Concentrations in the water sample were determined as follows:

$$\text{Found Concentration} = \mu g/L \text{ (eluate)} \times \frac{\text{volume (extract)}}{1000 \text{ mL}}$$

The target vs. found values were input as data to the Atlantic Research Corporation version of the USATHAMA detection limit program. The results are listed in Tables 40 and 41. The standard deviation and percent imprecision and inaccuracy are plotted in Figure 15 and 16. If all the data are used in the calcuations, a detection limit of 3.8 µg/L and correlation coefficient of 0.9801 are obtained. Upon dropping the 10 DL data, the detection limit is 1.42 µg/L with a correlation coefficient of 0.9901. The recovery of tetryl was essentially quantitative.

Table 41. Detection Limit Calculations for Tetryl via Solid Sorbent Tube Sampling

```
SUM(Y(i))=              49.6600
SUM(X(i))=              58.2900
SUM(X(i)↑2)=             264.5947
SUM(Y(i)↑2)=             209.7338
SUM(X(i)*Y(i))=                274.9876
X=          0.3202 Y +   0.2296    CORR. COEF.=  0.9901
Y=          1.0867 X +  -0.2495    CORR. COEF.=  0.9901

LINE      TC      C(FOUND)    C(CALC)      DELTA       GROUP
  1     0.0000     0.0200     -0.2495      0.2695      0.0000
  2     0.0000     0.0100     -0.2495      0.2595      0.0000
  3     0.0000     0.0000     -0.2495      0.2495      0.0000
  4     0.0000     0.0100     -0.2495      0.2595      0.0000
  5     0.7400     0.4900      0.5546     -0.0646      1.0000
  6     0.7400     0.4400      0.5546     -0.1146      1.0000
  7     0.7400     0.5900      0.5546      0.0354      1.0000
  8     0.7400     0.6100      0.5546      0.0554      1.0000
  9     1.4800     0.9700      1.3588     -0.3888      2.0000
 10     1.4800     1.1200      1.3588     -0.2388      2.0000
 11     1.4800     1.1500      1.3588     -0.2088      2.0000
 12     1.4800     1.2200      1.3588     -0.1388      2.0000
 13     2.9600     2.3700      2.9671     -0.5971      3.0000
 14     2.9600     2.9400      2.9671     -0.0271      3.0000
 15     2.9600     2.6100      2.9671     -0.3571      3.0000
 16     2.9600     3.6500      2.9671      0.6829      3.0000
 17     7.4000     7.4000      7.7921     -0.3921      4.0000
 18     7.3900     9.0000      7.7812      1.2188      4.0000
 19     7.3900     7.6200      7.7812     -0.1612      4.0000
 20     7.3900     7.4400      7.7812     -0.3412      4.0000
.........................................
STANDARD  ERROR OF ESTIMATE (Sxy) =              0.4174
N=          20.0000   n=            1.0000
TOTAL N=          20.0000
t=          1.7340
t BASED ON TOTAL N
UPPER CONFIDENCE LIMIT AT(X=0) =            0.5271


upper confidence line at X=            0.7400 is              1.3331
lower confidence line at X=            0.7400 is             -0.2138
STANDARD DEVIATION AT X=               0.7400  is             0.0810
PERCENT INACCURACY AT X=             0.7400  IS           -28.0405
PERCENT IMPRECISION AT X=            0.7400  IS            15.2082
MEAN FOUND AT  X=          0.7400  IS              0.5325

upper confidence line at X=            1.4800 is              2.1218
lower confidence line at X=            1.4800 is              0.5958
STANDARD DEVIATION AT X=               1.4800  is             0.1054
PERCENT INACCURACY AT X=             1.4800  IS           -24.6622
PERCENT IMPRECISION AT X=            1.4800  IS             9.4490
MEAN FOUND AT  X=          1.4800  IS              1.1150

upper confidence line at X=            2.9600 is              3.7279
lower confidence line at X=            2.9600 is              2.2064
STANDARD DEVIATION AT X=               2.9600  is             0.3764
PERCENT INACCURACY AT X=             2.9600  IS           -2.3814
PERCENT IMPRECISION AT X=            2.9600  IS            1
MEAN FOUND AT  X=          2.9600  IS              2.8925

upper confidence line at X=            7.3900 is              8.60.
lower confidence line at X=            7.3900 is              6.9611
STANDARD DEVIATION AT X=               7.3900  is             0.7827
PERCENT INACCURACY AT X=             7.3900  IS             5.4276
PERCENT IMPRECISION AT X=            7.3900  IS             8.6973
MEAN FOUND AT  X=          7.3900  IS              7.3650

|-----------------------------------------|
|  DETECTION LIMIT  =          1.4171 mg   |
|-----------------------------------------|
```

Table 42. Detection Limit Data Summary for Tetryl

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	.02	.01	.00	.01	.01	.01	0	
.74	.49	.44	.59	.61	.53	.08	15.2	-28.0
1.48	.97	1.12	1.15	1.22	1.12	.11	9.4	-24.7
2.96	2.37	2.94	2.61	3.65	2.89	.56	19.2	- 2.3
7.39	7.40	9.00	7.62	7.44	7.86	.76	9.7	6.4
14.78	10.52	14.01	16.04	15.90	14.12	2.57	18.2	- 4.5

Y = 0.978X - 0.0378; Detection Limit = 3.86 µg/L; Correlation Coefficient = 0.9801 for all data (0-10 DL)

Y = 1.0867X - 0.2495; Detection Limit = 1.42 µg/L; Correlation Coefficient = 0.9901 for (0-5 DL)

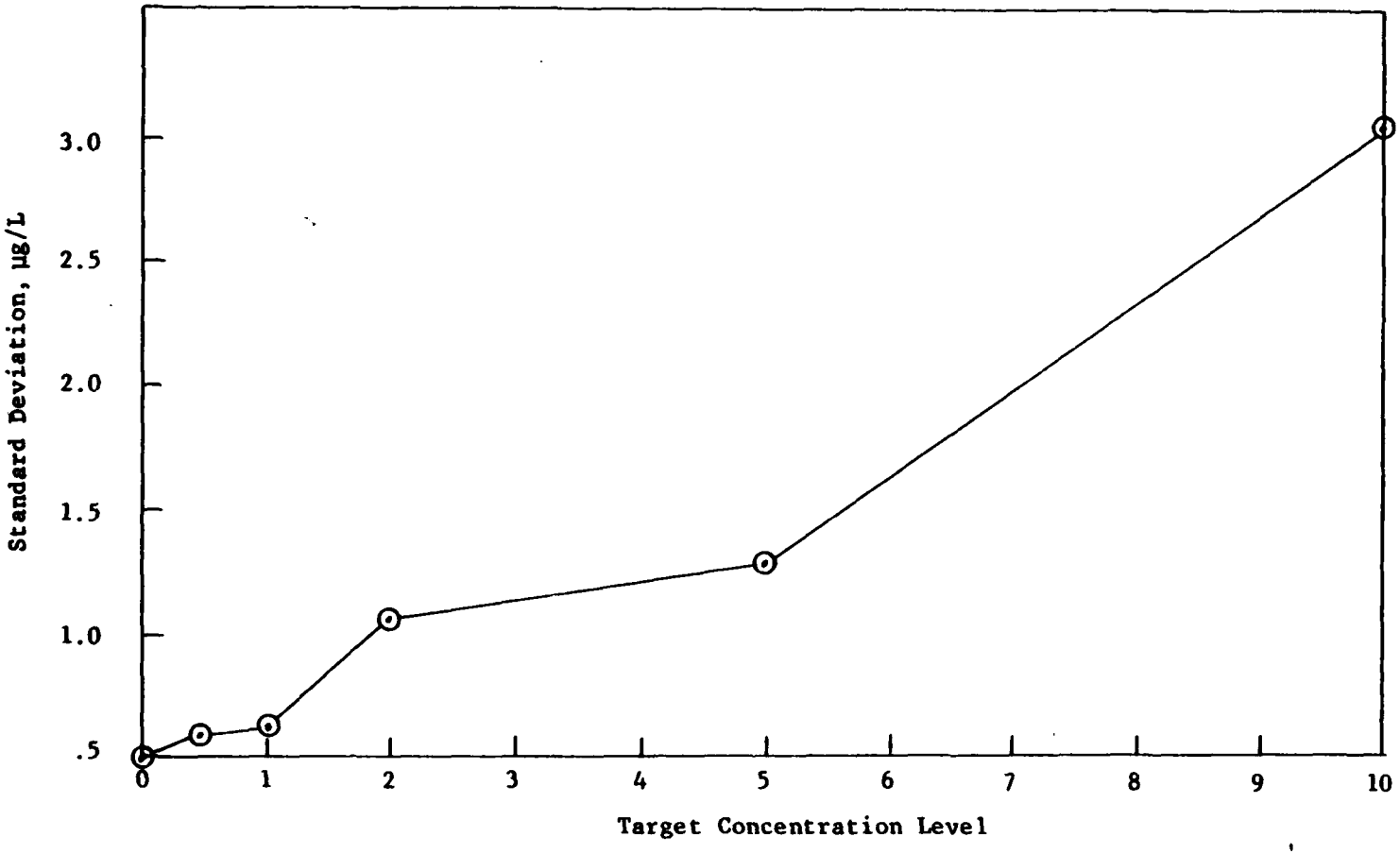


Figure 15. Standard Deviation - Tetryl Solid Sorbent Tube Sampling

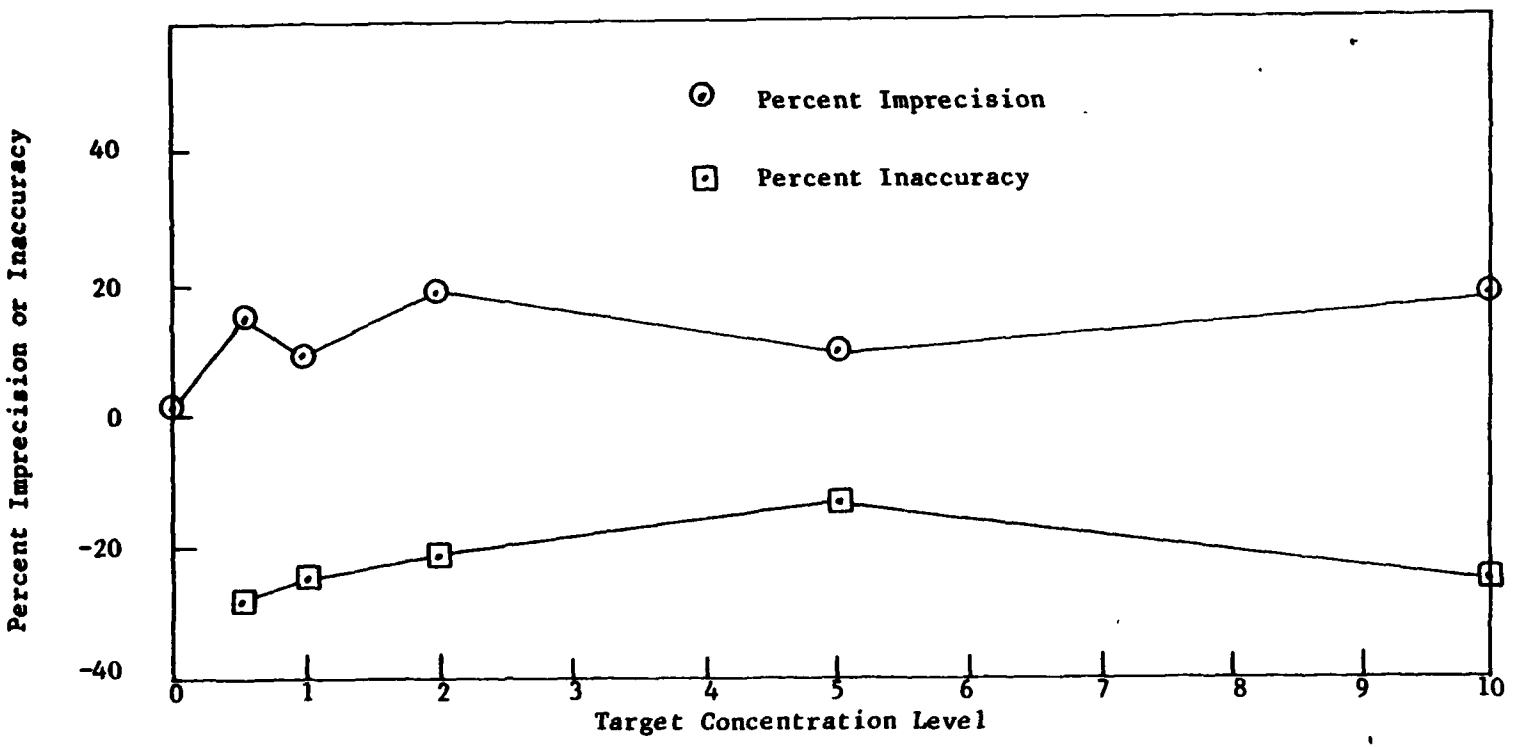


Figure 16. Percent Imprecision and Percent Inaccuracy - Tetryl Solid Sorbent Tube Sampling

C. Nitroglycerine and PETN on Porapak R

The method tested is described in detail in Appendix C. To perform the precision and accuracy testing, the Porapak R sorbent was prewashed with acetone by soxhlet extracton for two hours. After drying in a vacuum oven at 30°C for one hour, approximately 3 mL of the sorbent was packed into graduated disposable pipets and retained with wads of glass wool. The sorbent was then further-cleaned by pumping several hundred mL of acetone through each tube until HPLC analysis indicated that all impurities had been removed. The tubes were then conditioned by pumping 50 mL of distilled water through them.

For precision and accuracy testing, a stock solution was prepared in 10% acetonitrile/water which contained 8.56 mg/L of PETN and 8.45 mg/L of nitroglycerine. This solution was prepared fresh daily after disappearance of the PETN in the stock was repeatedly observed. Spiked samples for precision and accuracy testing were prepared from this stock by adding specified amounts to standard water. The concentrations of the spiked samples were:

Concentrated Level	PETN Concentration (µg/L)	Nitroglycerine Concentration (µg/L)
Blank	0	0
0.5 DL	2.57	2.54
1 DL	5.14	5.07
2 DL	10.3	10.1
5 DL	25.7	25.4
10 DL	51.4	50.7

This series of samples was tested daily for four days.

Sampling was accomplished by pumping each liter solution through a conditioned sorbent tube. The loaded sorbent tubes were blown dry for several minutes with a stream of nitrogen. Desorption was accomplished by attaching the loaded sorbent tube to the pump and pumping 20 mL of acetone through the tube. The first 20 drops of water were discarded and the next 20 mL of acetone were collected in a graduated cylinder. Four mL of the acetone eluate were blown to dryness under a stream of nitrogen and reconstituted with 2 mL of hexane.

HPLC analysis was used to quantitate the PETN and nitroglycerine in the eluate. The instrumentation used was a Perkin-Elmer LC-601 with a Perkin-Elmer LC-55 variable wavelength spectrometer, Perkin-Elmer LC-420 autosampler with rheodyne #7010 automated sampling valve and 200 µL sample loop. The following conditions were employed:

Column: Waters radial compression column (10 cm x 7) mm I.D.)
10 micron silica

Carrier Solvent: 2.5% isopropanol/97.5% hexane

Solvent Flow Rate: 2 mL/min.

UV Detector @ 204 nm

The concentrations of PETN and nitroglycerine in the original water were calculated according to the following formula:

$$\text{Found Concentration} = \frac{(\text{anal. conc.}) \times 20 \text{ mL eluate} \times 2 \text{ conc. in solv. exchange}}{1000 \text{ mL } H_2O}$$

The found and target values for the four-day study were input into the Atlantic Research Corporation version of the USATHAMA detection limit computer program. A summary of the data and the program printouts are shown in Tables 43 through 46. The standard deviation, percent inaccuracy and percent imprecision are plotted in Figures 17 through 20. Correlation coefficients of greater than 0.99 were obtained for both compounds. The detection limits were 8.96 µg/L and 6.94 µg/L for PETN and nitroglycerine, respectively. Detection limits could be further improved by additional concentration of the acetone eluate in the solvent exchange procedure. Recoveries of nitroglycerine and PETN were 68 and 82%, respectively. Although these recoveries were lowered than observed in the desorption and optimization studies, they were consistent. Problems were observed with decomposition of the PETN in the aqueous spiking stock. These problems were overcome by freshly preparing the solution at least once daily. Increased recoveries might be accomplished by using the reverse desorption techique.

D. Picric Acid on Porapak R

The method tested is detailed in Appendix C. To perform the precision and accuracy testing, the Porapak R sorbent was prewashed with acetone by soxhlet extraction for two hours. After drying in a vacuum oven at 30°C for one hour, approximately 3 mL of the sorbent was packed into graduated disposable pipets and retained with wads of glass wool. The sorbent was then further cleaned by pumping 50 mL of methanol containing 0.05M tetrabutylammonium hydroxide through each tube or until HPLC analysis indicated that all impurities had been removed. The tubes were then conditioned by pumping 50 mL of methanol and 50 mL of distilled water through them.

For precision and accuracy testing, a stock solution containing 1.04 mg of picric acid per liter of standard water was prepared. Spiked samples for precision and accuracy testing were prepared from this stock by adding specified amounts to standard water. The concentrations of the spiked samples were:

```
USATHAMA DETECTION LIMIT PROGRAM

SUM(Y(i))=              300.3800
SUM(X(i))=              380.4400
SUM(X(i)↑2)=          13766.2580
SUM(Y(i)↑2)=           3795.0644
SUM(X(i)*Y(i))=           7181.9936
X=          1.9312 Y +   -0.2722     CORR. COEF.=   0.9910
Y=          0.5179 X +    0.1409     CORR. COEF.=   0.9910

LINE      TC      C(FOUND)     C(CALC)      DELTA        GROUP
  1     0.0000      0.0000      0.1409     -0.1409       0.0000
  2     0.0000      0.0000      0.1409     -0.1409       0.0000
  3     0.0000      0.0000      0.1409     -0.1409       0.0000
  4     0.0000      0.0000      0.1409     -0.1409       0.0000
  5     2.5700      1.7100      1.4717      0.2383       1.0000
  6     2.5700      1.5700      1.4717      0.0983       1.0000
  7     2.5700      1.2300      1.4717     -0.2417       1.0000
  8     2.5700      1.3700      1.4717     -0.1017       1.0000
  9     5.1400      3.6800      2.8025      0.8775       2.0000
 10     5.1400      1.8500      2.8025     -0.9525       2.0000
 11     5.1400      2.5400      2.8025     -0.2625       2.0000
 12     5.1400      2.7300      2.8025     -0.0725       2.0000
 13    10.3000      6.8600      5.4744      1.3856       3.0000
 14    10.3000      5.0000      5.4744     -0.4744       3.0000
 15    10.3000      5.0600      5.4744     -0.4144       3.0000
 16    10.3000      4.9300      5.4744     -0.5444       3.0000
 17    25.7000     16.7400     13.4488      3.2912       4.0000
 18    25.7000     13.1500     13.4488     -0.2988       4.0000
 19    25.7000     13.8300     13.4488      0.3812       4.0000
 20    25.7000     12.0300     13.4488     -1.4188       4.0000
 21    51.4000     30.0800     26.7566      3.3234       5.0000
 22    51.4000     26.7900     26.7566      0.0334       5.0000
 23    51.4000     24.5900     26.7566     -2.1666       5.0000
 24    51.4000     24.6400     26.7566     -2.1166       5.0000
.....
STANDARD  ERROR OF ESTIMATE (Sxy) =          1.3132
N=          24.0000   n=          1.0000
TOTAL N=          24.0000
t=          1.7170
t BASED ON TOTAL N
UPPER CONFIDENCE LIMIT AT(X=0) =          2.4760


upper confidence line at X=          2.5700 is          3.7962
lower confidence line at X=          2.5700 is         -0.8528
STANDARD DEVIATION AT X=          2.5700  is          0.2123
PERCENT INACCURACY AT X=          2.5700  IS        -42.8016
PERCENT IMPRECISION AT X=          2.5700  IS         14.4414
MEAN FOUND AT  X=          2.5700  IS          1.4700

upper confidence line at X=          5.1400 is          5.1183
lower confidence line at X=          5.1400 is          0.4867
STANDARD DEVIATION AT X=          5.1400  is          0.7549
PERCENT INACCURACY AT X=          5.1400  IS        -47.4708
PERCENT IMPRECISION AT X=          5.1400  IS         27.3574
MEAN FOUND AT  X=          5.1400  IS          2.7000

upper confidence line at X=         10.3000 is          7.7783
lower confidence line at X=         10.3000 is          3.1706
STANDARD DEVIATION AT X=         10.3000  is          0.9332
PERCENT INACCURACY AT X=         10.3000  IS        -46.9660
PERCENT IMPRECISION AT X=         10.3000  IS         17.0834
MEAN FOUND AT  X=         10.3000  IS          5.4625

upper confidence line at X=         25.7000 is         15.7629
lower confidence line at X=         25.7000 is         11.1355
STANDARD DEVIATION AT X=         25.7000  is          2.0103
PERCENT INACCURACY AT X=         25.7000  IS        -45.7685
PERCENT IMPRECISION AT X=         25.7000  IS         14.4239
MEAN FOUND AT  X=         25.7000  IS         13.4375

upper confidence line at X=         51.4000 is         29.2298
lower confidence line at X=         51.4000 is         24.2834
STANDARD DEVIATION AT X=         51.4000  is          2.5824
PERCENT INACCURACY AT X=         51.4000  IS        -48.3949
PERCENT IMPRECISION AT X=         51.4000  IS          9.7356
MEAN FOUND AT  X=         51.4000  IS         26.7150

|-----------------------------------------|
|  DETECTION LIMIT  =          3.9631 µg/L
|-----------------------------------------|
```

Table 43. Detection Limit Calculations for PETN via Solid Sorbent Tube Sampling

Table 44. PETN Data Summary

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	0	0	0	0	0	0		
2.57	1.71	1.57	1.23	1.37	1.47	0.21	14.4	-42.8
5.14	3.68	1.85	2.54	2.73	2.70	0.75	28.0	-47.5
10.30	6.86	5.00	5.06	4.93	5.46	0.93	17.1	-47.0
25.7	16.74	13.15	13.83	12.03	13.94	2.01	14.4	-45.8
51.4	30.08	26.79	24.59	24.64	26.53	2.58	9.7	-48.4

.04

Y = 0.5178X + 0.1409

Correlation Coefficient = 0.9910

Detection Limit = 8.96µg/L

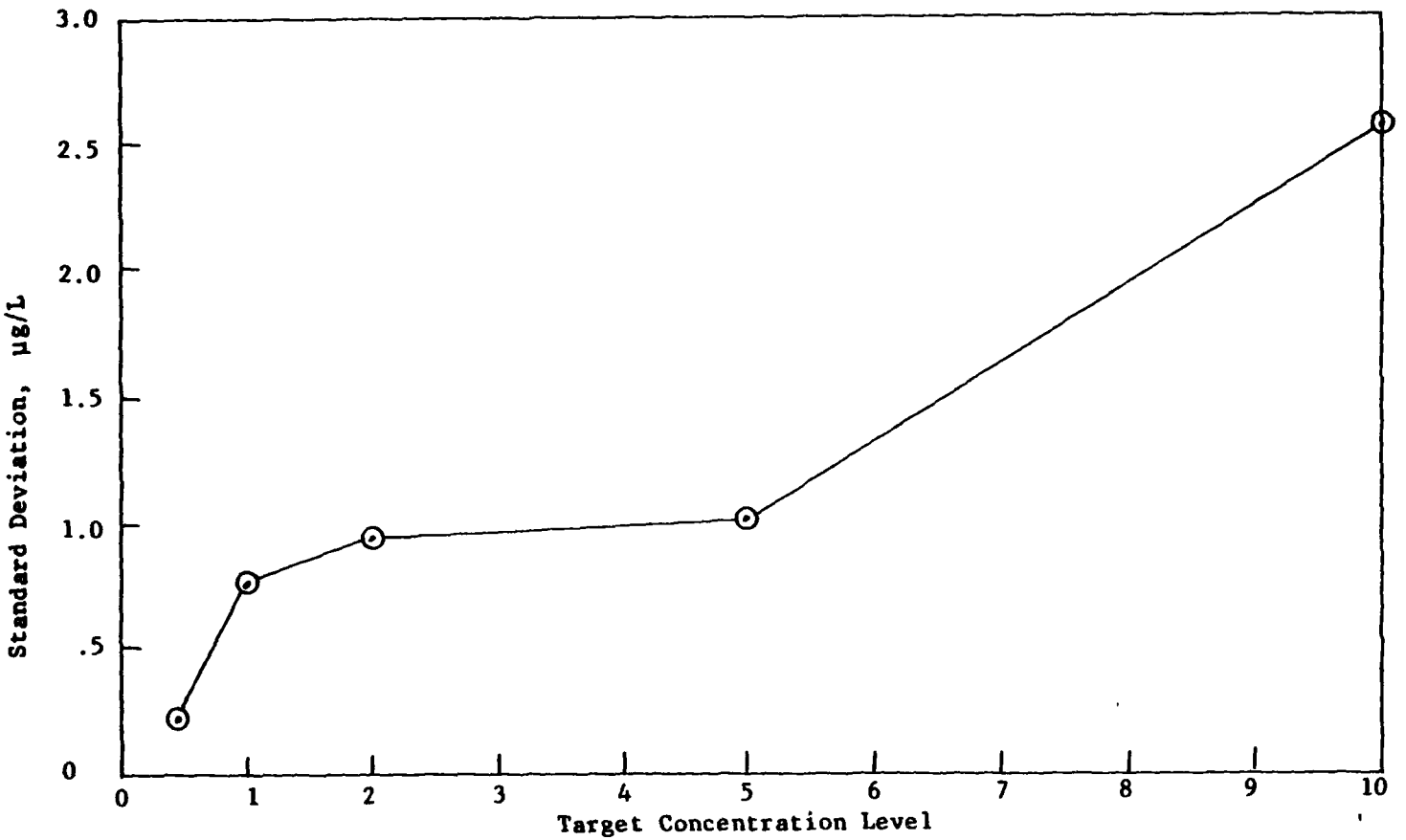


Figure 17. Standard Deviation - PETN Solid Sorbent Tube Sampling

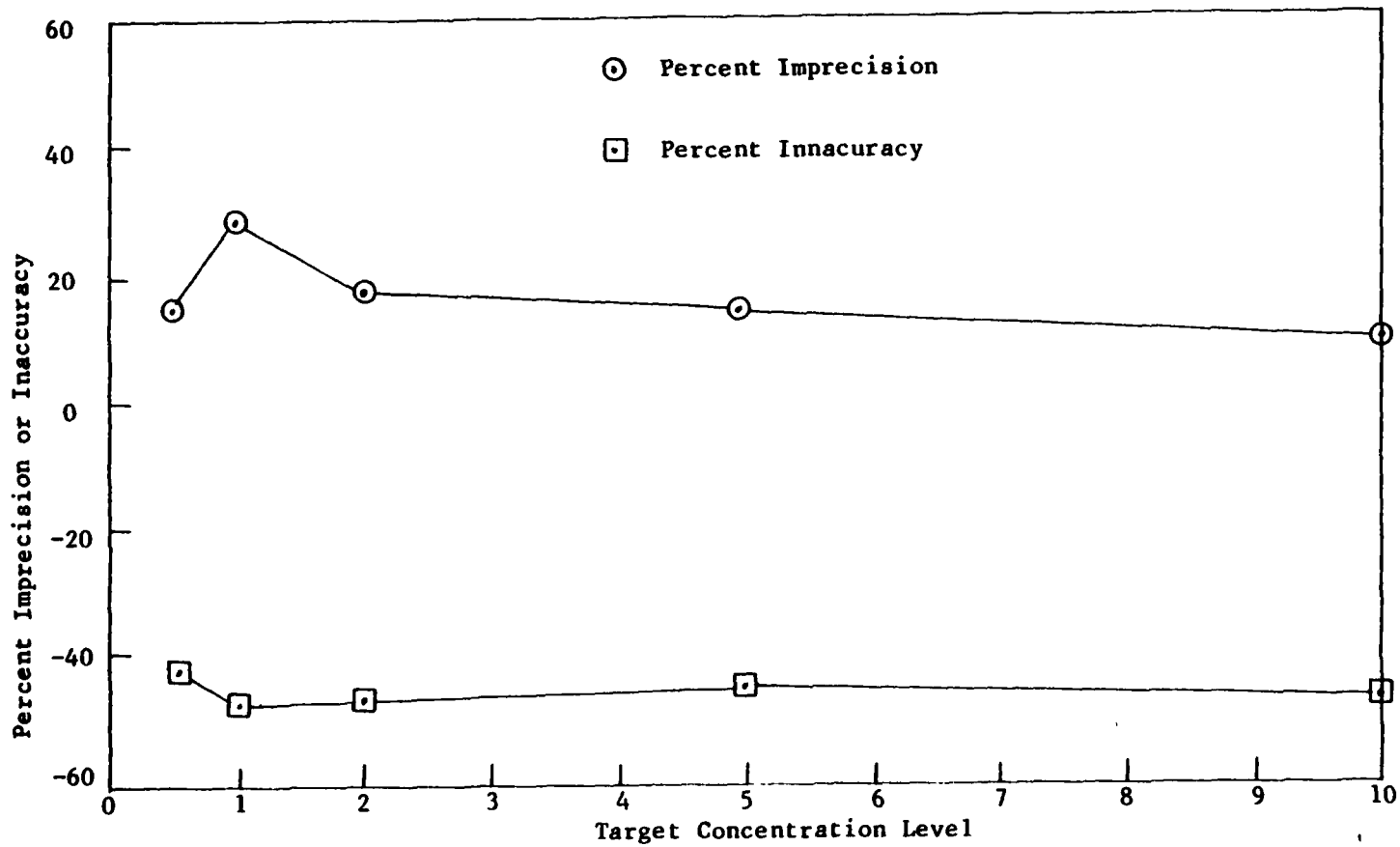


Figure 18. Percent Imprecision and Percent Inaccuracy - PETN Solid Sorbent Tube Sampling

```
SUM(Y(i))=              274.2900
SUM(X(i))=              375.2700
SUM(X(i))↑2=          13399.4193
SUM(Y(i))↑2=           6706.4185
SUM(X(i)*Y(i))=           9446.4995
X=          1.4603 Y +  -1.0530    CORR. COEF.=  0.9944
Y=          0.6843 X +   0.7211    CORR. COEF.=  0.9944

LINE      TC      C(FOUND)    C(CALC)      DELTA        GROUP
  1     0.0000      0.0000      0.7211     -0.7211      0.0000
  2     0.0000      0.0000      0.7211     -0.7211      0.0000
  3     0.0000      0.0000      0.7211     -0.7211      0.0000
  4     0.0000      0.0000      0.7211     -0.7211      0.0000
  5     2.5400      3.0700      2.4605      0.6095      1.0000
  6     2.5400      2.8100      2.4605      0.3495      1.0000
  7     2.5700      2.4100      2.4810     -0.0710      1.0000
  8     2.5400      2.5600      2.4605      0.0995      1.0000
  9     5.0700      4.1900      4.1930     -0.0030      2.0000
 10     5.0700      3.4200      4.1930     -0.7730      2.0000
 11     5.0700      4.4200      4.1930      0.2270      2.0000
 12     5.0700      4.0300      4.1930     -0.1630      2.0000
 13    10.1000      9.6600      7.6375      1.0225      3.0000
 14    10.1000      8.5100      7.6375      0.8725      3.0000
 15    10.1000      7.6500      7.6375      0.0125      3.0000
 16    10.1000      8.2500      7.6375      0.6125      3.0000
 17    25.4000     19.6600     18.1150      1.5450      4.0000
 18    25.4000     16.9300     18.1150     -1.1850      4.0000
 19    25.4000     19.9200     18.1150      1.8050      4.0000
 20    25.4000     17.0900     18.1150     -1.0250      4.0000
 21    50.7000     32.7300     35.4404     -2.7104      5.0000
 22    50.7000     39.1900     35.4404      3.7396      5.0000
 23    50.7000     35.5500     35.4404      0.1096      5.0000
 24    50.7000     33.2500     35.4404     -2.1904      5.0000
.....................................
STANDARD  ERROR OF ESTIMATE (Sxy) =              1.3431
N=          24.0000   n=          1.0000
TOTAL N=          24.0000
t=          1.7170
t BASED ON TOTAL N
UPPER CONFIDENCE LIMIT AT(X=0) =          3.1111


upper confidence line at X=          2.5400 is          4.3097
lower confidence line at X=          2.5400 is          0.3812
STANDARD DEVIATION AT X=          2.5400 is          0.2899
PERCENT INACCURACY AT X=          2.5400  IS          6.7913
PERCENT IMPRECISION AT X=          2.5400  IS         10.6865
MEAN FOUND AT  X=          2.5400  IS          2.7125

upper confidence line at X=          5.0700 is          6.5634
lower confidence line at X=          5.0700 is          1.8226
STANDARD DEVIATION AT X=          5.0700 is          0.4277
PERCENT INACCURACY AT X=          5.0700  IS        -20.6087
PERCENT IMPRECISION AT X=          5.0700  IS         10.6537
MEAN FOUND AT  X=          5.0700  IS          4.0150

upper confidence line at X=         10.1000 is          8.9358
lower confidence line at X=         10.1000 is          5.2793
STANDARD DEVIATION AT X=         10.1000 is          0.4451
PERCENT INACCURACY AT X=         10.1000  IS        -18.1436
PERCENT IMPRECISION AT X=         10.1000  IS          5.3843
MEAN FOUND AT  X=         10.1000  IS          8.2675

upper confidence line at X=         25.4000 is         30.4829
lower confidence line at X=         25.4000 is         15.7470
STANDARD DEVIATION AT X=         25.4000 is          1.6099
PERCENT INACCURACY AT X=         25.4000  IS        -27.5591
PERCENT IMPRECISION AT X=         25.4000  IS          8.7493
MEAN FOUND AT  X=         25.4000  IS         18.4000

upper confidence line at X=         50.7000 is         37.9717
lower confidence line at X=         50.7000 is         32.8090
STANDARD DEVIATION AT X=         50.7000 is          2.3362
PERCENT INACCURACY AT X=         50.7000  IS        -30.6154
PERCENT IMPRECISION AT X=         50.7000  IS          8.3469
MEAN FOUND AT  X=         50.7000  IS         35.1775

|-----------------------------------------|
|  DETECTION LIMIT  =          6.9437 mg/L|
|-----------------------------------------|
```

Table 45. Detection Limit Calculations for Nitroglycerine via Solid Sorbent Tube Sampling

Table 46. Nitroglycerine Data Summary

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	0	0	0	0	0	0	6.8	-10.7
2.54	3.07	2.81	2.41	2.56	2.71	0.29	10.7	-20.8
5.07	4.19	3.42	4.42	4.03	4.02	0.43	5.4	-18.1
10.10	8.66	8.51	7.65	8.25	8.27	0.45	8.7	-27.6
25.4	19.66	16.93	19.92	17.07	18.40	1.61	8.3	-30.62
50.7	32.73	39.18	35.55	32.55	35.18	2.94		

$Y = 0.684X + 0.7211$

Correlation Coefficient = 0.9944

Detection Limit = 6.94 µg/L

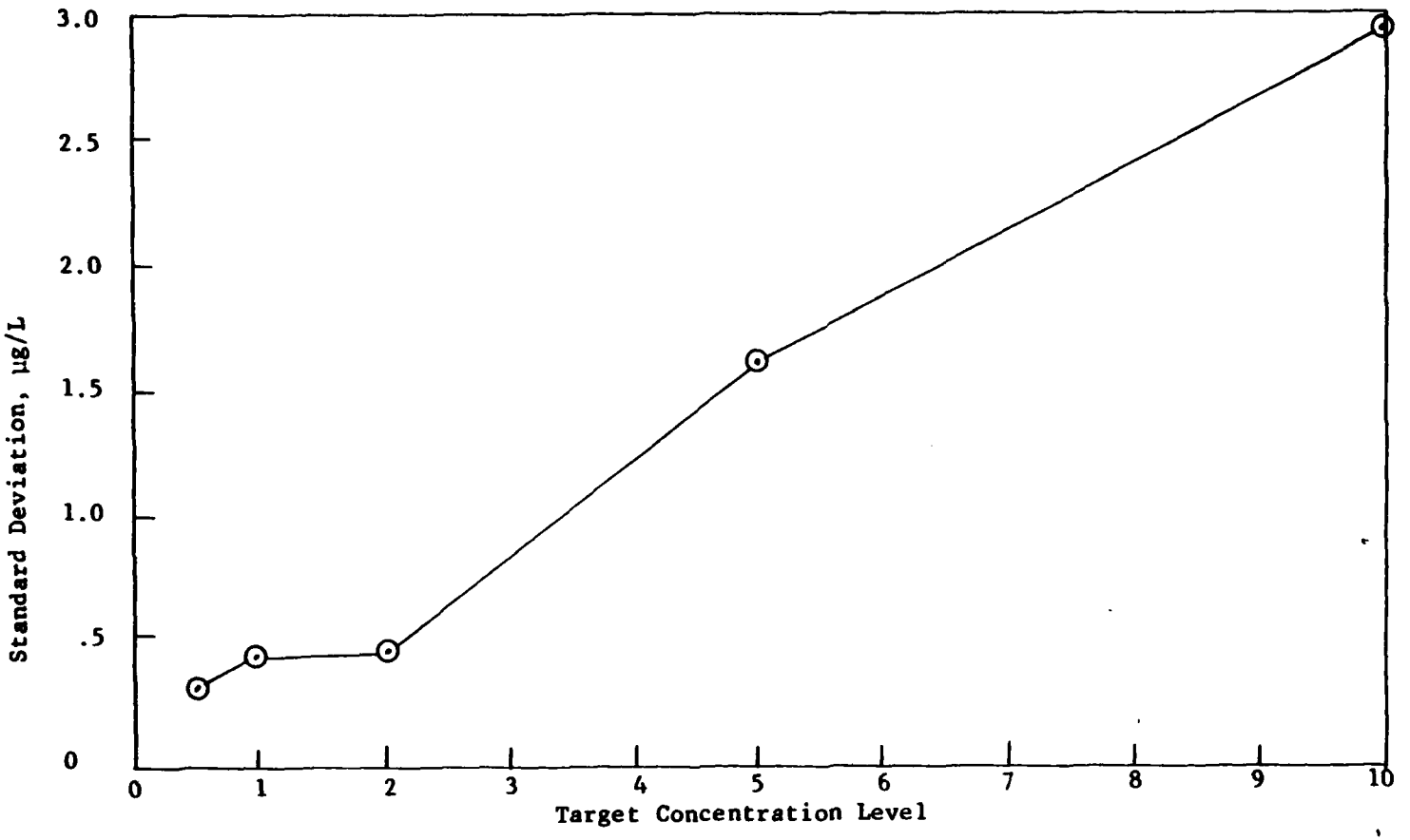


Figure 19. Standard Deviation - Nitroglycerine Solid Sorbent Tube Sampling

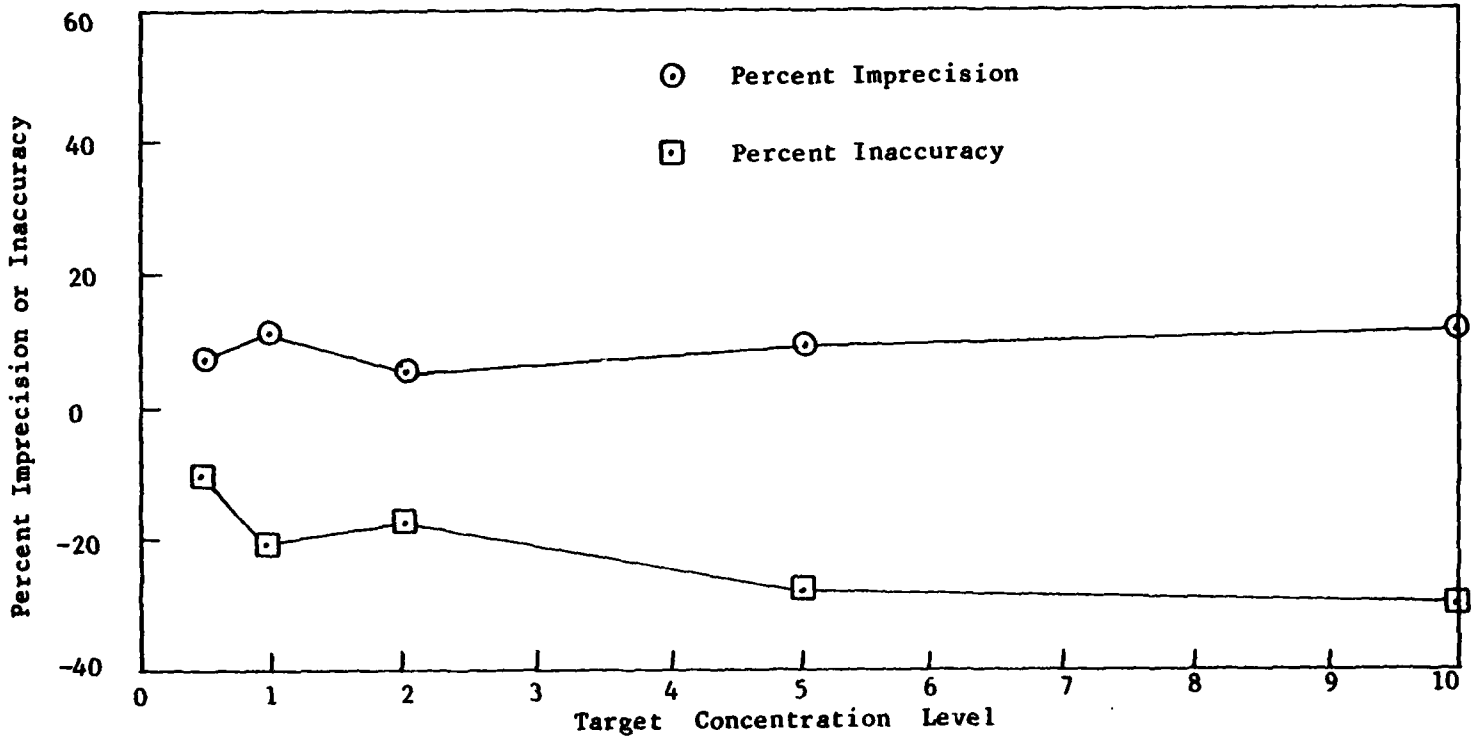


Figure 20. Percent Imprecision and Percent Inaccuracy - Nitroglycerine Solid Sorbent Tube Sampling

Concentration Level	Picric Acid Concentration, µg/L
Blank	0
0.5 DL	2.6
1 DL	5.2
2 DL	10.2
5 DL	26.0
10 DL	52.0

This series of samples was tested daily for four days.

Sampling was accomplished by pumping each liter solution through a conditioned sorbent tube. The loaded sorbent tubes were blown dry for several minutes with a stream of nitrogen. Desorption was accomplished by completely forcing two 3.75 mL portions of methanol containing 0.05M tetrabutylammonium hydroxide through each tube and collecting the 7.5 mL of eluate. Two drops of 1M H_3PO_4 and 12.5 mL of water are added to the eluate.

HPLC analysis was used to quantitiate the picric acid. A Perkin-Elmer LC-601 with a Perkin-Elmer LC-55 variable wavelength spectrophotometer and a Perkin-Elmer LC-420 autosampler with a rheodyne #7010 automated sampling valve and a 200 µL sample loop were used for the analysis. The following conditions were employed.

Column: Waters radial compression column (10 cm x 7 mm I.D.)
10 micron ODS

Carrier Solvent - 50% acetonitrile, 50% water, 0.005M tetra-butylammonium hydroxide buffered to pH 6.5

Solvent Flow Rate - 2.0 mL/min.

UV Detector @ 205 nm

The concentration of picric acid in the original water was calculated according to the following formula:

$$\text{Found Concentration} = \frac{\text{anal. conc. x 20 mL extract}}{\text{1000 mL } H_2O}$$

The found and target values for the four-day study were input into the Atlantic Research Corporation version of the USATHAMA detection limit computer program. A summary of the data and the program printouts are shown in Tables 47 and 48. The standard deviation, percent inaccuracy and percent imprecision are plotted in Figures 21 and 22. A correlation coefficient of 0.994 was obtained with a detection limit of 6.98 µg/L. The detection limit could be lowered by concentration of the methanol eluate and/or less dilution of the sample with water. Recovery of the picric acid was 56.5%. In comparison with the literature data on recovery of phenols form sorbents, this recovery of picric acid by the method is quite good. Increased recovery could be had by using the reverse desorption techique and further optimization of the desorption eluant.

```
          25.0000          9999.0000          9999.0000
SUM(Y(i)=          219.6650
SUM(X(i)=          384.8000
SUM(X(i)↑2=        14087.8400
SUM(Y(i)↑2=         4565.3369
SUM(X(i)*Y(i)=         7995.5980
X=          1.7700 Y +  -0.1667    CORR. COEF.=  0.9946
Y=          0.5650 X +   0.0942    CORR. COEF.=  0.9946

LINE      TC      C(FOUND)    C(CALC)      DELTA        IFOLF
  1     0.0000      0.0000      0.0942     -0.0942      0.0000
  2     0.0000      0.0000      0.0942     -0.0942      0.0000
  3     0.0000      0.0000      0.0942     -0.0942      0.0000
  4     0.0000      0.0000      0.0942     -0.0942      0.0000
  5     2.6000      1.0200      1.5631     -0.5431      1.0000
  6     2.6000      1.3800      1.5631     -0.1831      1.0000
  7     2.6000      1.0100      1.5631     -0.5531      1.0000
  8     2.6000      1.6100      1.5631      0.0469      1.0000
  9     5.2000      2.3800      3.0321     -0.6521      2.0000
 10     5.2000      2.3200      3.0321     -0.7121      2.0000
 11     5.2000      2.9700      3.0321     -0.0621      2.0000
 12     5.2000      3.5400      3.0321      0.5079      2.0000
 13    10.4000      4.9800      5.9700     -0.9900      3.0000
 14    10.4000      7.4500      5.9700      1.4800      3.0000
 15    10.4000      6.2400      5.9700      0.2700      3.0000
 16    10.4000      6.5900      5.9700      0.6200      3.0000
 17    26.0000     14.3600     14.7837     -0.4237      4.0000
 18    26.0000     16.6750     14.7837      1.8913      4.0000
 19    26.0000     15.2400     14.7837      0.4563      4.0000
 20    26.0000     15.4000     14.7837      0.6163      4.0000
 21    52.0000     28.2100     29.4732     -1.2632      5.0000
 22    52.0000     32.4900     29.4732      3.0168      5.0000
 23    52.0000     28.8500     29.4732     -0.6232      5.0000
 24    52.0000     26.9500     29.4732     -2.5232      5.0000
.....
STANDARD ERROR OF ESTIMATE (Sxy) =              1.1138
N=          24.0000   n=          1.0000
TOTAL N=          24.0000
t=          1.7170
t BASED ON TOTAL N
UPPER CONFIDENCE LIMIT AT(X=0) =          2.0761


upper confidence line at X=          2.6000 is          3.5361
lower confidence line at X=          2.6000 is         -0.4099
STANDARD DEVIATION AT X=          2.6000  is          0.2926
PERCENT INACCURACY AT X=          2.6000  IS        -51.7308
PERCENT IMPRECISION AT X=         2.6000  IS         23.3172
MEAN FOUND AT  X=          2.6000  IS          1.2550

upper confidence line at X=          5.2000 is          4.9977
lower confidence line at X=          5.2000 is          1.0665
STANDARD DEVIATION AT X=          5.2000  is          0.5725
PERCENT INACCURACY AT X=          5.2000  IS        -46.1058
PERCENT IMPRECISION AT X=         5.2000  IS         20.4232
MEAN FOUND AT  X=          5.2000  IS          3.0035

upper confidence line at X=         10.4000 is          7.9255
lower confidence line at X=         10.4000 is          4.0145
STANDARD DEVIATION AT X=         10.4000  is          1.0250
PERCENT INACCURACY AT X=         10.4000  IS        -39.2788
PERCENT IMPRECISION AT X=        10.4000  IS         16.2307
MEAN FOUND AT  X=         10.4000  IS          6.1150

upper confidence line at X=         26.0000 is         16.7472
lower confidence line at X=         26.0000 is         12.8202
STANDARD DEVIATION AT X=         26.0000  is          0.9542
PERCENT INACCURACY AT X=         26.0000  IS        -40.6971
PERCENT IMPRECISION AT X=        26.0000  IS          6.1885
MEAN FOUND AT  X=         26.0000  IS         15.4156

upper confidence line at X=         52.0000 is         31.5724
lower confidence line at X=         52.0000 is         27.3739
STANDARD DEVIATION AT X=         52.0000  is          2.3781
PERCENT INACCURACY AT X=         52.0000  IS        -43.9904
PERCENT IMPRECISION AT X=        52.0000  IS          8.1653
MEAN FOUND AT  X=         52.0000  IS         29.1250

|-----------------------------------------|
|  DETECTION LIMIT  =          6.9797 mg/L|
|-----------------------------------------|
```

Table 47. Detection Limit Calculations for Picric Acid via Solid Sorbent Tube Sampling

Table 48. Detection Limit Data Summary for Picric Acid

Target Concentration (µg/)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	0	0	0	0	0	0		
2.60	1.02	1.38	1.01	1.61	1.26	0.30	23.3	-51.7
5.20	2.38	2.32	2.97	3.54	2.80	0.57	20.4	-46.1
10.40	4.98	7.45	6.24	6.59	6.32	1.03	16.2	-39.3
26.00	14.36	16.67	15.24	15.40	15.42	0.95	6.1	-40.7
52.00	28.21	32.49	28.85	26.95	29.13	2.38	8.2	-44.0

Y = 0.5650X + 0.0942

Correlation Coefficient = 0.9946

Detection Limit = 6.98 µg/L

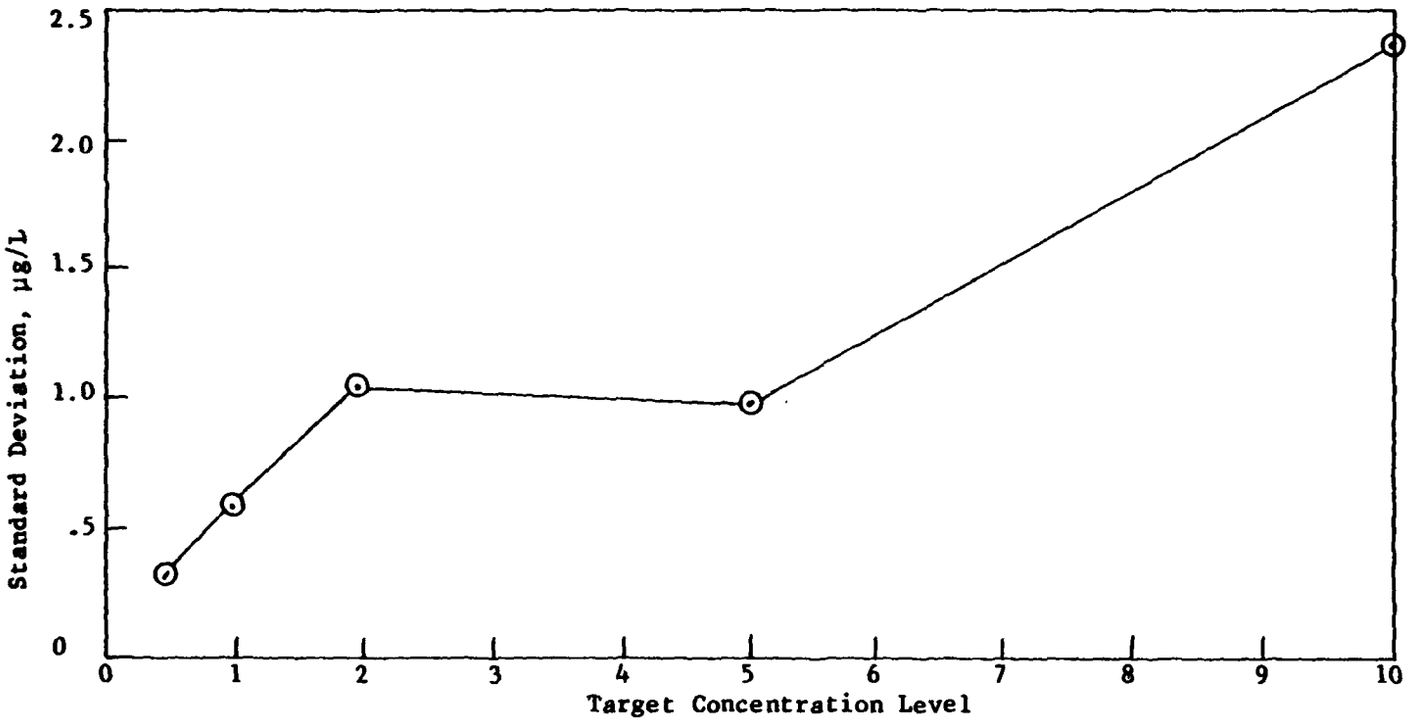


Figure 21. Standard Deviation - Picric Acid Solid Sorbent Tube Sampling

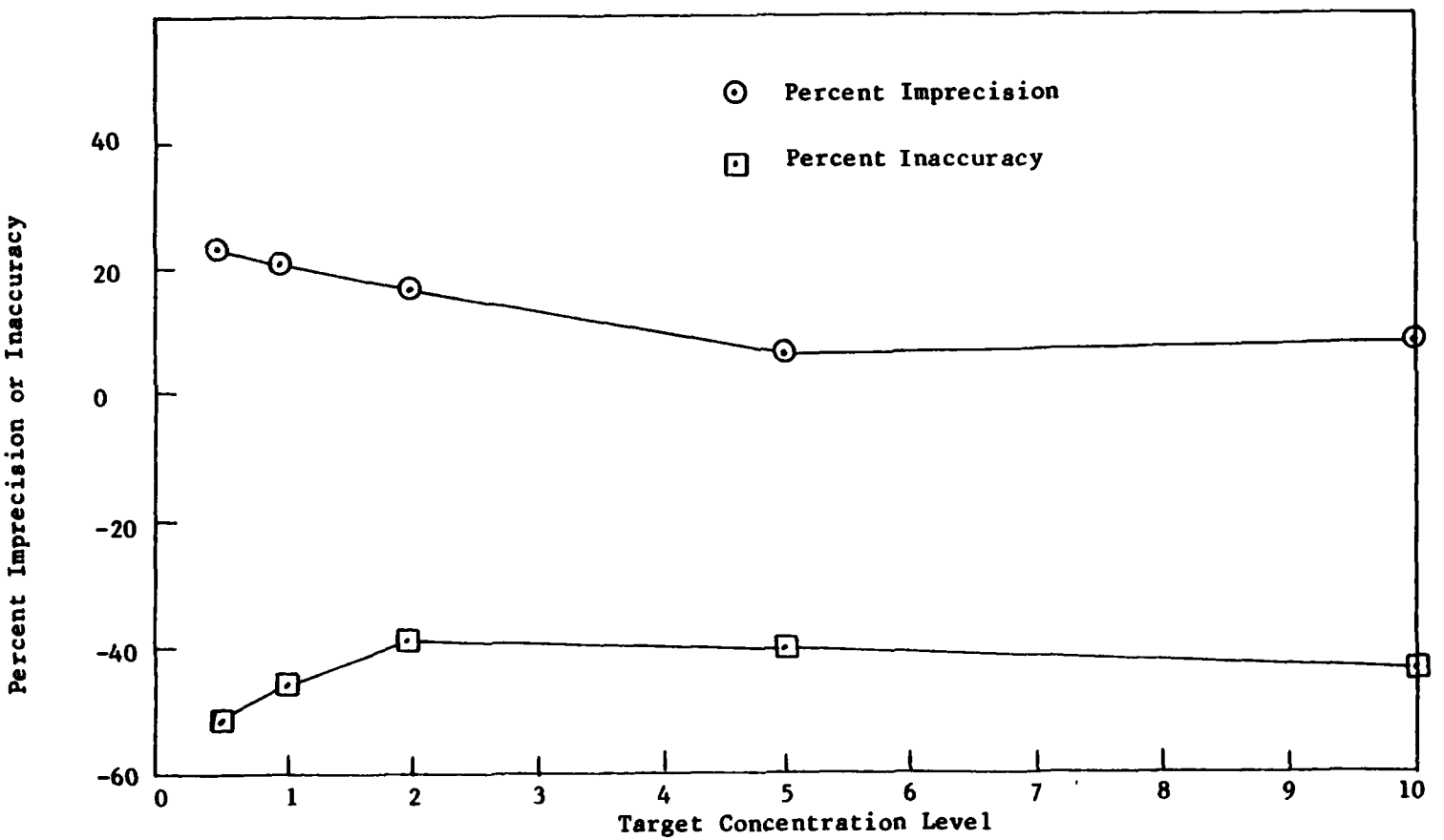


Figure 22. Percent Imprecision and Percent Inaccuracy - Picric Acid Solid Sorbent Tube Sampling

V. PRESERVATION STUDIES

As discussed in Section III.B.7 (p. 60) the initial preservation tests evaluated a variety of storage conditions. The results of these initial preservation tests with TNT and the DNT's are compiled in Table 49. As can be observed from the table, low recoveries of all explosives were found when the tubes were subjected to a heat cycle or exposed to light. Drying the tubes with nitrogen and leaving them open during storage, also resulted in low recoveries of the explosives. However, wet sorbent maintained in open tubes in the dark at 4°C or nitrogen dried, sealed tubes maintained in the dark at 4°C yielded good recoveries of all explosives except 2,6-DNT. The preservation studies with the nitrotoluene explosives were repeated to determine if the low recoveries of 2,6-DNT were real. For these repeat tests and subsequent preservation studies with other explosives/sorbent combinations, only cold and room temperature storage conditions were evaluated. All loaded tubes were simply wrapped in aluminum foil and stored.

The results of the preservations studies are presented in Table 50 through 52. All adsorption, desorptions and analyses were performed according to the methods compiled in Appendix C. For the nitrotoluenes and RDX storage at 4°C recoveries of the explosives were generally high and relatively consistent. Only the 2,6-DNT recoveries were lower than observed when the tubes were desorbed on the same day (quantitative for same day desorption versus 90% recovery for stored tubes). Recoveries from tubes stored at room temperature were more variable than those stored at 4°C.

Recoveries of PETN and nitroglycerine from tubes stored at 4°C were higher than observed for same day desorption. No explanations for this higher recovery is readily apparant. Additional studies would have to be conducted to determine if this is an anomaly or if better recoveries are possible if these tubes are allowed to set for several days. In contrast to the high recoveries observed for the tubes stored at 4°C, room temperature storage resulted in usually low and variable recoveries of PETN and nitroglycerine.

The tetryl tubes were stored for a much longer period of time (60 days versus 22 and 27 days) than the nitrotoluene or nitrate ester tubes due to a backlog on the gas chromatographs. In general, the recoveries of tetryl were highest for those tubes stored at 4°C and lowest for the tubes stored at room temperature. The cold storage #2 tube probably started to dry out and the tetryl degraded.

In general, cold storage of the loaded sorbent tubes indicated acceptable recoveries of the explosives for periods up to 30 days. Long storage of the loaded tubes may be possible but recoveries have not been established. Due to time constraints, repeat of the tetryl storage studies and picric acid storage studies were not conducted. In addition, storage of a capped tubes (with teflon plugs) should be further investigated.

Table 49. Initial Preservation Studies with the Nitrotoluenes

Environmental Conditions*	% Recovery		
	TNT	2,4-DNT	2,6-DNT
Wet - 4°C - Open - Dark	102	75.3	21.3
N_2 Dried - 4°C - Sealed - Dark	105	71.2	40.9
N_2 Dried - 4°C - Open - Dark	76	73.2	36.7
Wet - Heat Cycle - Open - Dark	38	37.6	34.3
Wet - Ambient - Open - Sunlight	26	53.9	22.5

*Preservation Time = 22 days

Table 50. Preservation Studies with TNT, 2,4-DNT, 2,6-DNT and RDX on Porapak S

Environmental Conditions*	TNT Target Conc. (µg/L)	TNT Found Conc. (µg/L)	TNT Recovery	2,4-DNT Target Conc. (µg/L)	2,4-DNT Found Conc. (µg/l)	2,4-DNT Recovery	2,6-DNT Target Conc. (µg/L)	2,6-DNT Found Conc. (µg/L)	2,6-DNT Recovery	RDX Target Conc. (µg/L)	RDX Found Conc. (µg/L)	RDX Recovery
Room Temperature (70°F)	7.1	7.15	100.7	7.1	8.25	116.2	9.25	8.65	93.5	9.34	6.47	69.3
Room Temperature (70°C)	7.1	7.05	99.3	7.1	8.65	121.8	9.25	9.2	99.5	9.34	8.42	90.2
Room Temperature (70°C)	7.1	2.65	37.3	7.1	4.15	58.5	9.25	3.25	35.1	9.34	4.74	50.8
4°C (Refrigerator)	7.1	6.95	97.9	7.1	7.5	105.6	9.25	8.65	93.5	9.34	9.02	96.6
4°C (Refrigerator)	7.1	6.75	95.1	7.1	6.75	95.1	9.25	8.4	90.8	9.34	9.02	96.6
4°C (Refrigerator)	7.1	6.8	95.8	7.1	6.4	90.1	9.25	7.9	85.4	9.34	9.17	98.2

*Preservation Time = 27 days

Table 51. Preservation Studies with PETN and Nitroglycerine on Porapak R

Environmental Conditions*	PETN			Nitroglycerine		
	Target Concentration (µg/L)	Found Concentration (µg/L)	% Recovery	Target Concentration (µg/L)	Found Concentration (µg/L)	% Recovery
Room Temperature (70°F)	25.7	10.3	40.1	25.4	7.04	27.7
Room Temperature (70°F)	25.7	10.2	39.7	25.4	21.8	85.8
4°C (Refrigerator)	25.7	21.3	82.9	25.4	21.4	84.1
4°C (Refrigerator)	25.7	19.0	73.9	25.4	21.7	85.5

*Preservation Time = 22 days

Table 52. Preservation Studies with Tetryl

Environmental Conditions	Target Conc. (µg/L)	Found Conc. (µg/L)	% Recovery
Room Temperature, 70°F	7.39	5.50	74.4
Room Temperature, 70°F	7.39	4.10	55.5
Room Temperature, 70°F	7.39	3.60	48.7
4°C (Refrigerator)	7.39	6.00	81.2
4°C (Refrigerator)	7.39	4.10	55.5
4°C (Refrigerator)	7.39	6.40	86.6

VI. CONCLUSIONS AND RECOMMENDATIONS

Thirteen resins have been evaluated for their applicability to sampling and concentration of eight explosives from water for quantitative analysis. The optimum resin, adsorption/desorption technique and analytical method for each explosive were chosen after a series of screening studies. The total method (sampling through analysis) was then subjected to four-day precision and accuracy testing. These methods are summarized in Table 53.

Several interesting conclusions can be drawn from the data generated during this study:

1) The Porapak resins (R or S) generally outperformed the styrene divinylbenzene resins (e.g. XAD-4, XAD-2) for sampling and concentration of these explosives from water for quantitative analysis. Only in the case of tetryl did XAD-4 prove superior to the Porapak resins.

2) The solid sorbent sampling and concentration technique yielded near quantitative recoveries of TNT, 2,6-DNT, RDX and tetryl. Recoveries of 2,4-DNT were 85%. Nitroglycerine, PETN and picric acid recoveries were 68%, 52% and 57%, respectively. However, the recoveries were very consistent over the 20 fold concentration range tested.

3) The solid sorbent sampling and concentration technique can be used to detect TNT, 2,4-DNT, 2,6-DNT, RDX, tetryl, PETN, nitroglycerine and picric acid in water at concentrations less than 10 µg/L. Lower detection limits are possible with sight modifications of the methods.

4) Inorganics and particulates in the water to be sampled do not interfere with the collection, concentration or analysis of the explosives. Several samples of nitroglycerine and PETN spiked into a turbid well water containing high concentrations of iron, calcium and carbonate were evaluated in parallel with spiked standard water (distilled water containing 1.48 g Na_2SO_4 and 1.65 g NaCl per liter) samples. The particulates in the well water were collected in the glass wool on top of the resin column. No difference in recoveries were found between the two waters. The only adverse effect observed was the pumping rate of the turbid well water through the sorbent tube was less than that for standard water.

5) Significant interferences have been observed from monomers and other compounds remaining on the resins from the manufacturing process. These interferences are extremely bad when HPLC analysis is used with UV detection at wavelengths below 230 nm. Interferences in the resin can be eliminated by thorough washing of the resin before sampling.

Table 53. Summary of Solid Sorbent Explosives Sampling and Analysis Methods

Explosive	Sorbent	Desorption Solvent	Analysis Method	Detection Limit (µg/L)	Recovery
TNT	Porapak S	Acetone	GC-EC	1.50	93
2,4-DNT	Porapak S	Acetone	GC-EC	1.69	85
2,6-DNT	Porapak S	Acetone	GC-EC	0.97	100
RDX	Porapak S	Acetone	Solvent Exchange to CH_2Cl_2 HPLC-UV @ 232 nm	0.64	99
Tetryl	XAD-4	Methanol Benzene	GC-EC	1.42	98
PETN	Porapak R	Acetone	Solvent Exchange to hexane HPLC-UV @ 204 nm	8.96	52
Nitroglycerine	Porapak R	Acetone	Solvent Exchange to hexane HPLC-UV @ 204 nm	6.94	68
Picric Acid	Porapak R	0.05M tetrabutyl-ammonium hydroxide methanol	HPLC-UV @ 205 nm	6.98	57

6) Organics in environmental waters could be a problem if sorbent tubes are used for sampling and concentration. The organics could interfere with the adsorption of the explosives, could initiate in situ reactions on the resin or could interfere with the analysis of explosives. The extent of interferences of this type still remains to be determined.

7) The explosives loaded onto the resins remain stable for a period of at least three weeks if the resins remain moist and the tubes are protected from light and stored at 4°C. Recoveries of the explosives at the end of 3 weeks are approximately the same as if they were immediately desorbed from the resin. The only exceptions were 2,6-DNT and tetryl. Only 90% of the 2,6-DNT was recovered after three weeks storage compared to quantitative recovery with immediate desorption. For tetryl, recoveries averaged only 74%, however, storage was for 60 days compared to less than 30 days for the other compounds.

8) Sorbent tubes can be reused after regeneration and cleaning without loss of collection efficiencies. Reuse of the resin cuts the material cost associated with solid sorbent sampling to about $0.32 a sample if the sorbent tube is reused 20 times compared to $2.78 per sample if the tube is used only once:

Inital tube set-up or 1 use	
5 mL pipet	$0.205
sorbent (3cc)	2.20
cleaning solvent (100 mL)	0.37
price for the sample	$2.775
Reuse 20 times	
initial	$2.775
20xRegeneration (50 mL)	
=185x20 =	3.70
total of 20 times	$6.475
price per sample	$0.32

We have not observed carryover or loss of adsorption/desorption efficiency with tubes used up to 30 times.

9) In general, the solid sorbents sampling and analysis methods for TNT, 2,4-DNT, 2,6-DNT, RDX, tetryl, PETN, nitroglycerine and picric acid appears to be a big step forward for analysis of low levels of these explosives in ground water. The procedures are easy to perform and inexpensive. The necessity of carrying large sampling bottles into the field is eliminated. Also the expense of shipping bulky samples and the problems of decomposition of the explosives in the sample are eliminated.

For field sampling, the only requirements are a small sampling pump and associated tubes (similar to the FMI-LAB pump model #SS50-1296), the sorbent tubes and ring stand, watch, aluminum foil and a small cooler (6-pack size). A volumetric flask can also be included if the pump does not have an accurately calibrated delivery rate. The entire set-up can be easily transported in a small suitcase. Electricity for operation of the pump can be obtained from a car battery.

The next step in the development of the sorbent tube sampling and analysis methods is actual field sampling trials. Atlantic Research Corporation recommends that sampling of ground waters for explosives be conducted at a minimum of two Army inststallations. Conventional sampling techniques should also be conducted so that the results of the two techniques can be compared.

The use of solid sorbent sampling tubes for tetracene and lead styphnate was not evaluated under the contract since suitable analytical methods for these explosives were not available. Atlantic Research Corporation evaluated various analytical methodologies for tetracene. We did have preliminary success for this compound using HPLC, however, time and monies did not permit further development of the method. We recommend that further work be devoted to development of a tetracene analysis method and that a solid sorbent sampling method be developed for this explosive.

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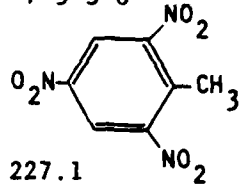
APPENDIX A

Selected Physical, Chemical and Toxicological Properties of the Explosives Evaluated

Sources: Department of the Army, 1967; Meyer, 1977; Sax, 1975

TNT

CAS Name:	2-methyl-1,3,5-trinitrobenzene
CAS Registry No.:	118-96-7
Common Names:	trinitroluol, trotyl, tolite
Molecular Formula:	$C_7H_5N_3O_6$
Molecular Structure:	
Molecular Weight:	227.1
Melting Point:	80.8°C
Density (solid):	1.654 g/cm^3
Density (melt):	1.47 g/cm^3
Specific Heat:	0.331 kcal/kg
Heat of Explosion:	1210 kcal/kg
Impact Sensitivity:	1.5 kp m
Detonation Velocity:	6900 m/s
Boiling Point:	190°C at 2 mm Hg
	245 - 250°C at 50 mm Hg
Vapor Pressure:	0.057 millibars @ 81°C
	0.14 millibars @ 100°C
	4 millibars @ 150°C
	14 millibars @ 200°C
	86.5 millibars @ 250°C

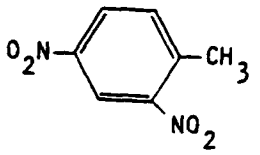
Solubility:

	0°	20°C	50°C
H_2O (g/100 g)	0.010	0.013	0.1475
ethanol (g/100 g)	0.65	1.23	4.61
ethyl ether (g/100 g)	1.73	3.29	-
acetone (g/100 g)	57	109	246
chloroform (g/100 g)	6	19	150
ethylene chloride (g/100 g)	-	18.7	97
benzene (g/100 g)	13	67	284
toluene (g/100 g)	28	55	208

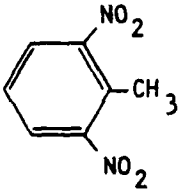
Toxicity:	Symptoms include dermatitis, cyanosis, gastritis, acute yellow atrophy of the liver and aplastic anemia.
Toxicity Routes:	skin absorption, inhalation, ingestion
TLV:	1.5 mg/m^3

DINITROTOLUENE

CAS Name:	(1) 1-methyl-2,4-dinitrobenzene
	(2) 2-methyl-1,3-dinitrobenzene
CAS Registry No.:	(1) 121-14-2
	(2) 606-202-2
Common Names:	(1), (2) dinitrotoluene, DNT, dinitrotoluol
Molecular Formula:	$C_7H_6N_2O_4$
Molecular Weight:	182.1
Structural Formula:	(1)



(2)



Melting Point:	(1) 70.5°C
	(2) -
Density:	(1) 1.521 g/cm^3
	(2) 1.538 g/cm^3
Heat of Explosion:	(1) 1056 kcal/kg
	(2) 1085 kcal/kg
Impact Sensitivity:	no reaction up to 5 kp m
Vapor Pressure	(1) 0.014 millibars @ 35°C
	0.11 millibars @ 70°C
	0.83 millibars @ 100°C
	8.5 millibars @ 150°C
	50.5 millibars @ 200°C
	223 millibars @ 250°C
	300 millibars @ 300°C

Solubility:	sparingly soluble in water, alcohol and ethyl ether. Soluble in acetone and benzene
Toxicity:	route - skin absorption, inhalation, ingestion. Symptoms include headache, fatigue, nausea, vomiting, marked chest pain, weight loss, jaundice and secondary anemia.
TLV:	1.5 mg/m^3; potential carcinogen

RDX

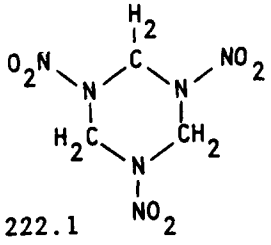
CAS Name: hexahydro-1,3,5-trinitro-1,3,5-triazine

CAS Registry No.: 121-82-4

Common Names: trimethylenetrinitramine, hexogen, cyclonite
cyclo-1,3,5-triethylene-2,4,6-trinitramine

Molecular Formula: $C_6H_6N_6O_6$

Molecular Structure:



Molecular Weight: 222.1

Melting Point: 204°C

Density: 1.816

Specific Heat: 0.30 kcal/kg

Heat of Explosion: 1439 kcal/kg

Impact Sensitivity: 0.75 kp m

Detonation Velocity: 8750 m/s

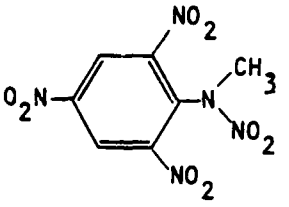
Vapor Pressure: 0.00054 millibars @ 110°C
0.0014 millibars @ 121°C
0.0034 millibars @ 131°C
0.0053 millibars @ 138.5°C

Solubility:

	20°C	50°C	96°C
H_2O (g/100 g)	0.0076	-	0.196
acetone (g/100 g)	7.4	12.8	
cyclohexanone (g/100 g)	-	-	25
methyl acetate (g/100 g)	2.95	6.0	
ethanol (g/100 g)	0.105	0.370	
ethyl ether (g/100 g)	0.055		
chloroform (g/100 g)	0.008		
benzene (g/100 g)	0.045	0.115	

Toxicity: low - some cases of epiliptiform seizures have been reported

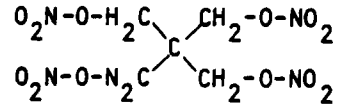
TETRYL

CAS Name:	N-methyl-N-2,4,6-tetranitroaniline
CAS Registry No.:	479-45-8
Common Names:	2,4,6-trinitrophenylmethylnitramine
Molecular Formula:	$C_7H_5N_5O_8$
Molecular Structure:	
Molecular Weight:	287.1
Melting Point:	129.5°C
Density:	1.73 g/cm^3
Specific Heat:	.217 kcal/kg
Heat of Explosion:	1320 kcal/kg
Impact Sensitivity:	0.3 kp m
Detonation Velocity:	7570 m/s
Solubility:	H_2O (g/100 g) 0.0075 @ 20°C 0.0195 @ 50°C 0.035 @ 60°C 0.081 @ 80°C

	20°C	60°C
ethanol (g/100 g)	0.563	2.64
carbon tetrachloride	0.025	0.154
chloroform (g/100 g)	0.57	2.65
ethyl chloride (g/100 g)	3.8	18.8
carbon disulfide (g/100 g)	0.021	
ethyl ether (g/100 g)	0.418	

Toxicity: major symptom is dermatitis

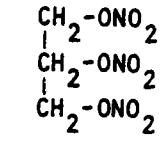
PETN

CAS Name:	2,2-bis(hydroxmethyl)-1,3-propanediol-tetranitrate
CAS Registry No.:	78-11-5
Common Names:	pentaerythrol tetranitrate, nitropenta, etc.
Molecular Formula:	$C_5H_8N_4O_{12}$
Molecular Structure:	
Molecular Weight:	316.1
Melting Point:	141.3°C
Density:	1.76 g/cm^3
Specific Heat:	0.26 kcal/kg
Heat of Explosion:	1408 kcal/kg
Impact Sensitivity:	0.3 kp
Detonation Velocity:	8400 m/s
Boiling Point:	160°C @ 2 mm Hg 180°C @ 50 mm Hg
Vapor Pressure:	0.0011 millibars @ 97.0°C 0.0042 millibars @ 110.6°C 0.015 millibars @ 121.0°C 0.050 millibars @ 131.6°C 0.094 millibars @ 138.8°C
Solubility H_2O (g/100 g)	0.0043 @ 25°C 0.018 g @ 96°C

	20°C	50°C
methanol (g/100 g)	0.46	1.87
ethanol (g/100 g)	0.11	0.71
ethyl ether (g/100 g)	0.25	-
acetone (g/100 g)	25.4	56.6
benzene (g/100 g)	0.3	2.05
toluene (g/100 g)	0.23	1.11
carbon tetrachloride (g/100 g)	0.10	0.12
methyl acetate	12.9	28.0
cyclohexanol (g/100 g)	-	0.5

Toxicity: Symptoms similar to nitroglycerine - headache, weakness, decline in blood pressure.

NITROGLYCERINE

CAS Name:	propanetrioltrinitrate
CAS Registry No.:	55-63-0
Common Names:	glycerol trinitrate; nitroglycerol, etc.
Molecular Formula:	$C_3H_5N_3O_9$
Molecular Structure:	
Molecular Weight:	227.1
Solidification Point:	13.2°C (stable - dipyramidal rhombic)
	2.2°C (unstable - triclinic)
Density (d_4^{20}):	1.591 g/cm^3
Index of Refraction (N_D^{20}):	1.4732
Specific Heat:	0.32 kcal/kg
Heat of Explosion:	1510 kcal/kg
Impact Sensitivity:	0.02 kp m
Detonation Velocity:	7600 m/s
Boiling Point:	125°C @ 2 mm Hg
	180°C @ 50 mm Hg
	145°C decomposes @ 760 mm Hg
Vapor Pressure:	0.00033 millibars @ 20°C
	0.0097 millibars @ 50°C
	0.13 millibars @ 80°C
	0.31 millibars @ 90°C
Solubility:	H_2O (g/100 g) 0.173 @ 20°C
	0.191 @ 30°C
	0.228 @ 50°C
	0.246 @ 60°C

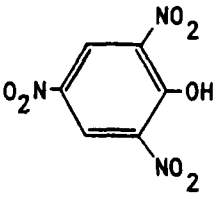
Ethanol (g/100 g) 7.5 @ 0°C
54 @ 20°C

Miscible with: hot ethanol, ethyl ether, acetone, glacial acetic acid, ethyl acetate, benzene, toluene, phenol, nitrobenzene, chloroform, ethyl chloride and nitric acid esters

Toxicity:

Routes - skin absorption; ingestion, inhalation.
Acute - symptoms include nausea, vomiting, headache, delerium, bradycardia, paralysis, convulsions, methemoglobinemia, cyanosis, circulatory collapse, death
Chronic - severe headache, hallucinations, skin rashes.

PICRIC ACID

CAS Names:	2,4,6-trinitrophenol
CAS Registry No.:	88-89-1
Common Names:	picric acid, melinite, byddite, pertite, shimose
Molecular Formula:	$C_6H_3N_3O_7$
Molecular Structure:	
Molecular Weight:	229.1
Solidification Point:	122.5°C
Density:	1.767 g/cm^3
Specific Heat:	0.254 kcal/kg
Impact Sensitivity:	0.75 kp m
Detonation Volocity:	7350 m/s
Vapor Pressure:	0.01 millibars @ 122°C 2.7 millibars @ 195°C 67 millibars @ 255°C
Solubility:	H_2O 1.4 g/100 g @ 20°C 6.8 g/100 g @ 100°C Soluble in benzene, sulfuric acid, nitric acid ethyl ether 2.0 g/100 g @ 20°C ethanol 6.2 g/100 g @ 20°C
Toxicity:	causes allergic reactions and irritative dermatitis; systemic symptoms include nausea, vomiting, diarrhea, suppressed urine, yellow coloration of skin and convulsions.

APPENDIX B

Detection Limit - QC for

Explosives from Water

A. Analysis of Low Levels of 2,4-DNT and 2,6-DNT in Water - Quantitative
USATHAMA Approval Number 1A

1. Application

Method used to determine the concentration of 2,4-DNT and 2,6-DNT in water using gas chromatography:

a. Tested Concentration Range: (µg/L)

2,4-DNT	0.260 to 5.20	µg/L
2,6-DNT	0.252 to 5.04	µg/L

b. Sensitivity:

2,4-DNT 128.3 area units/pg based on a 33.28 pg injection
2,6-DNT 247.5 area units/pg based on a 32.36 pg injection

c. Detection Limit: (µg/L)

2,4-DNT	0.91	µg/L
2,6-DNT	0.81	µg/L

d. Interferences: No interferences were observed with 2,4-DNT or 2,6-DNT.

e. Analysis Rate: Extraction requires 15 minutes to complete. GC analysis requires 5 minutes. One analyst can extract and analyze 25 - 30 samples per 8-hour day if a GC autoinjector is used.

2. Chemistry

$C_7H_6N_2O_4$	Toluene, 2,4-Dinitro
CAS RN	121-14-2
Melting Point:	71°C
Boiling Point:	300°C, Partially Decomposes

$C_7H_6N_2O_4$	Toluene, 2,6-Dinitro-
CAS RN	606-20-2
Melting Point:	66°C
Boiling Point:	Not available

Hazards. Use caution in handling these compounds; explosive hazard and toxic hazards exist.

3. Apparatus

a. Instrumentation:

Gas Chromatograph - Hewlett-Packard 5880A with computer controller and integrator, autoinjector and electron capture detector.

b. Parameters:

Column - 1.5% SP-2250/1.95% SP-2401 on 100/120 Supelcoport packed in a 2 mm I.D., 0.25 in O.D. by 6 ft. glass column.
Temperature - Injection port - 210°C
Oven - 160 - 200°C
Detector - 300°C
Temperature Programming - 8°C/min
Carrier Gas - Nitrogen at 28 cc/min.
Detector - Electron capture
Injection Volume - 2 µL
Retention Time - 2,4-DNT 1.71 min
2,6-DNT 1.32 min

c. Glassware/Hardware:

Volumetric Flask - 100 mL (10)
Volumetric Flask - 25 mL (2)
Volumetric Flask - 10 mL (12)
Pipet - 2 mL (1)
Pipet - 5 mL (1)
Pipet - 10 mL (7)
Culture tube with teflon-lined screw cap, 6 mm x 150 mm (6)
GC autosampler vials with teflon inserts (10)
Centrifuge
Aluminum foil
Refrigerator
10 µL Hamilton syringe (1)

d. Chemicals:

2,4-DNT "SARM" - PA 362, Lot #28493-A
2,6-DNT "SARM" - PA 363, Lot #31640-A
Benzene, certified (Fisher Scientific)
Methanol, certified (Fisher Scientific)
Standard Water - distilled water containing 100 mg/L each of sulfate and chloride.

4. Standards:

A concentrated stock solution of 2,4-DNT and 2,6-DNT is prepared by weighing out the following amounts of SARM materials into a volumetric flask and bringing to volume with methanol.

I	=	2,4-DNT	10.40 mg in 100 mL	=	104.0 mg/L
		2,6-DNT	10.08 mg in 100 mL	=	100.8 mg/L

Dilute stock solutions are prepared in methanol according to the following scheme:

II	=	5.0 mL of I to 100 mL	=	52.0 mg/L 2,4-DNT 50.4 mg/L 2,6-DNT
III	=	0.5 mL of I to 100 mL	=	0.520 mg/L 2,4-DNT 0.504 mg/L 2,6-DNT
IV	=	10 mL of II to 100 mL	=	0.052 mg/L 2,4-DNT 0.050 mg/L 2,6-DNT

The volumetric flasks are wrapped in aluminum foil and stored in the refrigerator until needed. Storage time should not exceed two months.

a. Calibration Standards: Calibration standards were prepared from the dilute stock solutions by diluting with benzene according to the following scheme:

A.	0.5 mL of II to 25 mL	=	104 µg/L 2,4-DNT 101 µg/L 2,6-DNT
B.	Dilute Stock III	=	520 µg/L 2,4-DNT 504 µg/L 2,6-DNT
C.	1 mL of A to 10 mL	=	104 µg/L 2,4-DNT 101 µg/L 2,6-DNT
D.	0.4 mL of A to 25 mL	=	16.6 µg/L 2,4-DNT 16.1 µg/L 2,6-DNT
E.	2 mL of C to 10 mL	=	3.33 µg/L 2,4-DNT 3.23 µg/L 2,6-DNT

b. Control Spikes: Control spikes are prepared by diluting the dilute stock solution with standard water according to the following scheme:

A.	0.5 mL of IV to 100 mL	=	0.26 µg/L 2,4-DNT 0.25 µg/L 2,6-DNT

B. 1.0 mL of IV to 100 mL = 0.52 µg/L 2,4-DNT
0.50 µg/L 2,6-DNT

C. 2.0 mL of IV to 100 mL = 1.04 µg/L 2,4-DNT
1.01 µg/L 2,6-DNT

D. 0.5 mL of III to 100 mL = 2.60 µg/L 2,4-DNT
2.52 µg/L 2,6-DNT

E. 1.0 mL of III to 100 mL = 5.20 µg/L 2,4-DNT
5.04 µg/L 2,6-DNT

F. Blank

5. Procedure

Pipet 15 mL of water sample into a new centrifuge tube. Pipet 0.5 mL of benzene into the tube, screw on the cap and shake well. Centrifuge the tube for 2 minutes. With a micropipet, carefully remove the benzene layer and place it directly into a GC autosampler vial. Add a second 0.5 mL aliquot of benzene to the water sample, shake and centrifuge. Remove the benzene layer and combine with first extract in the GC autosampler vial.

The samples are ready for analysis. Inject 2 µL of the 1000 µg/L standard on the column to prepare the column.

Inject 2 µL of the extract onto the GC column in duplicate.

Run standards singly at the beginning and end of each run.

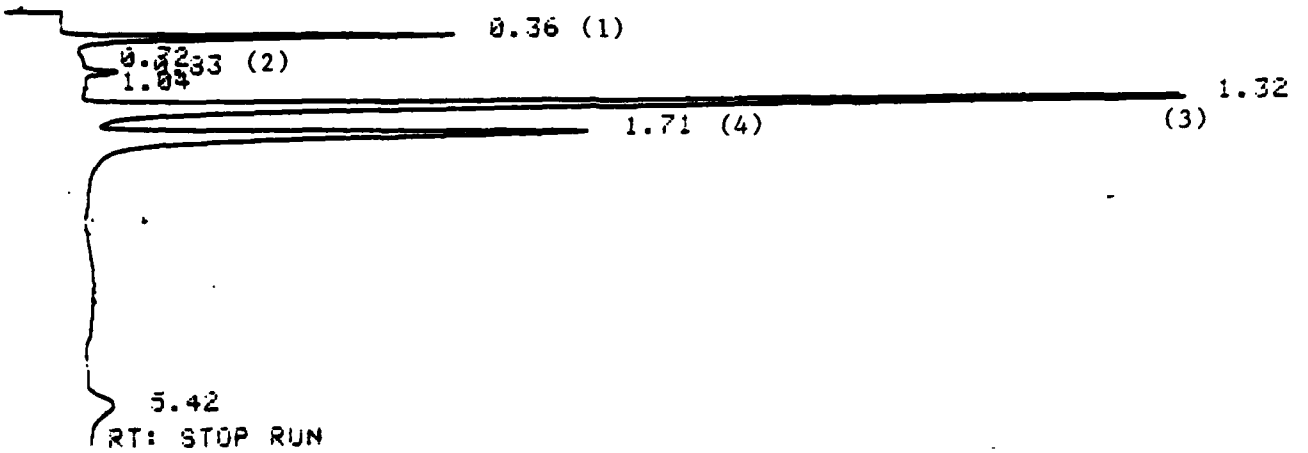
Plot peak area versus concentration to obtain standard curves for 2,4-DNT and 2,6-DNT. A typical spectrum is presented in Figure B-1.

6. Calculations

A linear regression equation is generated from the peak area versus 2,4-DNT or 2,6-DNT concentrations of the standards (Equations 1 and 2).

$$\text{slope} = b_1 = \frac{\Sigma x_i y_i - \frac{(\Sigma x_i)(\Sigma y_i)}{n}}{\Sigma x_i^2 - \frac{(\Sigma x_i)^2}{n}} \qquad \text{(Eq. 1)}$$

$$\text{intercept} = b_o = \frac{\Sigma y - b_1(\Sigma x)}{n} \qquad \text{(Eq. 2)}$$



PEAKS

1 - Solvent Benzene
2 - Impurity
3 - 2,4-DNT = 71 µg/L
4 - 2,6-DNT = 92.5 µg/L

Retention Time - 2,4-DNT = 1.32 min.
2,6-DNT = 1.71 min.

Instrumentation - Gas Chromatograph - Hewlett-Packard 5880A with
Computer Controller and Integrator
Auto Injector
Electron Capture Detector

Column - 1.5% SP-2250/1.95% SP-2401 on 100/120 Supelcoport packed in a 2 mm I.D., 0.25 in. O.D. by 6 ft. glass column

Temperature - Injection port - 210°C
Oven - 160-200°C
Detector - 300°C

Temperature Programming - 8°C/min.

Injection Volume - 2 µL

Carrier Gas - N_2 @ 28 cc/min.

Figure B-1. Chromatograph of 2,4-DNT and 2,6-DNT

The duplicate injections of a given detection limit spike are averaged and the found concentration is calculated from Equation 3.

$$\frac{\left[\frac{PA_1 + PA_2}{2} \quad b_1\right] + b_o}{16.67^*} = \text{found concentration} \qquad \text{(Eq. 3)}$$

PA = peak area
* = concentration factor

These calculations were performed on the data for each of the four days. The raw data and calculations are presented in Tables B-1 - 10. The found versus target concentrations for the four days were evaluated for their detection limit by the Hubaux and Vos (1975) formulae. In addition, the data were analyzed for standard deviation (Equation 4), percent imprecision (Equation 5), and percent inaccuracy (Equation 6). The detection limits for 2,4-DNT and 2,6-DNT are 0.91 and 0.81 µg/L, respectively.

$$\text{standard deviation} = s = \left[\frac{n\Sigma x^2 - (\Sigma x)^2}{n(n-1)}\right]^{1/2} \qquad \text{(Eq. 4)}$$

$$\text{percent imprecision} = s/\bar{x} \times 100 \qquad \text{(Eq. 5)}$$

$$\text{percent inaccuracy} = \frac{\bar{x} - \text{ppb added}}{\text{ppb added}} \times 100 \qquad \text{(Eq. 6)}$$

TABLE B-1. 2,4-DNT

Day 1 Data

Standards		Peak Area of Spiked Samples				
Concentration µg/L	Peak Area	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	435	829	16.67	0.10	0
3.328	1212	2540	1896	16.67	0.51	0.26
16.64	3801	4550	3860	16.67	1.05	0.52
104	42583	6043	6330	16.67	1.32	1.04
		21962	21711	16.67	3.42	2.6
		38822	39056	16.67	5.75	5.2

TABLE B-2. 2,4-DNT

Day 2 Data

Standards		Peak Area of Spiked Samples				
Concentration µg/L	Peak Area	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	0	325	16.67	0.03	0
3.328	1292	2423	2256	16.67	0.42	0.26
16.64	5099	3535	3451	16.67	0.66	0.52
104	42305	6183	6036	16.67	1.14	1.04
		16013	16147	16.67	2.54	2.6
		36037	35914	16.67	5.36	5.2

TABLE B-3. 2,4-DNT

Day 3 Data

Standards		Peak Area of Spiked Samples				
Concentration µg/L	Peak Area	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	93	125	16.67	0.03	0
3.328	775	2229	2121	16.67	0.54	0.26
16.64	4089	4801	4016	16.67	1.07	0.52
104	50193	7380	7419	16.67	1.28	1.04
		19766	19702	16.67	2.78	2.6
		39926	39901	16.67	5.07	5.2

TABLE B-4. 2,4-DNT

Day 4 Data

Standards		Peak Area of Spiked Samples				
Concentration µg/L	Peak Area	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	0	0	16.67	0.00	0
3.328	816	2999	2461	16.67	0.67	0.26
16.64	4088	5041	4395	16.67	1.07	0.52
104	49249	8071	8022	16.67	1.40	1.04
		22835	21891	16.67	3.12	2.6
		37849	39826	16.67	5.03	5.2

TABLE B-5. 2,4-DNT

Data Summary

Target Concentration (μg/L)	Found Concentration (μg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	0.10	0.03	0.03	0.00				
0.26	0.51	0.42	0.54	0.67	0.54	0.10	19.3	105.8
0.52	1.05	0.66	1.07	1.07	0.96	0.20	21.0	85.1
1.04	1.32	1.14	1.28	1.40	1.29	0.11	8.5	23.6
2.60	3.42	2.54	2.78	3.12	2.97	0.39	13.0	14.0
5.20	5.75	5.36	5.07	5.03	5.30	0.33	6.3	2.0

Y = 0.9839X + 0.2708

Y = 2,4-DNT levels in μg/L

X = peak area units

Correlation coefficient = 0.9909

Detection limit = 0.91 μg/L

TABLE B-6. 2,6-DNT

Day 1 Data

Standards		Peak Area of Spiked Samples				
Concentration µg/L	Peak Area	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	363	413	16.67	0.03	0
3.226	2310	3576	2886	16.67	0.20	0.25
16.13	7680	6765	6311	16.67	0.80	0.50
100.8	74287	10638	10931	16.67	1.20	1.01
		34889	35520	16.67	3.07	2.52
		64337	64839	16.67	5.31	5.04

TABLE B-7. 2,6-DNT

Day 2 Data

Standards		Peak Area of Spiked Samples				
Concentration µg/L	Peak Area	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	149	92	16.67	0.01	0
3.226	1926	3727	3406	16.67	0.38	0.25
16.13	8770	5950	5529	16.67	0.625	0.50
100.8	74633	11113	10288	16.67	1.12	1.01
		28157	28221	16.67	2.46	2.52
		59782	59941	16.67	4.90	5.04

TABLE B-8. 2,6-DNT

Day 3 Data

Standards		Peak Area of Spiked Samples				
Concentration µg/L	Peak Area	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	76	73	16.67	0.01	0
3.226	1573	4031	3952	16.67	0.49	0.25
16.13	7952	7637	6886	16.67	0.88	0.50
100.8	86941	13705	13059	16.67	1.22	1.01
		33038	32881	16.67	2.58	2.52
		68599	68761	16.67	4.87	5.04

Table B-9. 2,6-DNT

Day 4 Data

Standards		Peak Area of Spiked Samples				
Concentration µg/L	Peak Area	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	68	79	16.67	0.01	0
3.226	1672	4360	4148	16.67	0.53	0.25
16.13	7532	7490	7890	16.67	0.97	0.50
100.8	94071	14516	14366	16.67	1.37	1.01
		37128	35192	16.67	2.65	2.52
		66189	68596	16.67	4.48	5.04

TABLE B-10. 2,6-DNT

Data Summary

Target Concentration (μg/L)	Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	0.03	0.01	0.01	0.01				
0.252	0.20	0.38	0.49	0.53	0.40	0.15	36.9	58.7
0.504	0.80	0.625	0.88	0.97	0.82	0.15	17.9	62.5
1.01	1.20	1.12	1.22	1.37	1.23	0.10	8.5	21.8
2.52	3.07	2.46	2.58	2.65	2.69	0.27	9.9	6.7
5.04	5.31	4.90	4.87	4.48	4.89	0.34	6.9	-3.0

$Y = 0.9449X + 0.2052$

Y = 2,6-DNT levels in μg/L

X = peak area units

Correlation coefficient = 0.9923

Detection limit = 0.81 μg/L

B. Analysis of Low Levels of TNT in Water - Quantitative
USATHAMA Approval Number 1A

1. Application

Method used to determine the concentration of TNT in water.

a. Tested Concentration Range: (µg/L)

0.335 to 6.7 µg/L

b. Sensitivity:

457 area units/pg based on a 6.7 pg injection

c. Detection Limit:

0.85 µg/L

d. Interferences: Minor interferences were encountered which could be attributed to the presence of phthalate esters or other plasticizers.

e. Analysis Rate: Extraction requires 15 minutes to complete. GC analysis requires 5 minutes. One analyst can extract and analyze 25 - 30 samples per 8-hour day if a GC autoinjector is used.

2. Chemistry

$C_7H_5N_3O_6$	Toluene, 2,4,6-Trinitro-
CAS RN	118-96-7
Melting Point:	80.75°C
Boiling Point:	240°C (explodes)

Hazards. Use caution in handling this compound; explosive and toxic hazards exist.

3. Application

a. Instrumentation:

Gas Chromatograph - Hewlett-Packard 5880A with computer controller and integrator, autoinjector and electron capture detector.

b. Parameters:

Column - 1.5% SP-2250/1.95% SP-2401 on 100/120 Supelcoport packed in a 2 mm I.D., 0.25 in O.D. by 6 ft. glass column
Temperature - injection port - 210°C
oven - 180°C
detector - 300°C
Temperature Programming - isothermal
Carrier Gas - nitrogen at 28 cc/min
Detector - electron capture
Injection Volume - 2 μl
Retention Time - 3.23 min.

c. Glassware/Hardware:

Volumetric Flask - 100 mL (10)
Volumetric Flask - 25 mL (2)
Pipet - 2 mL (1)
Pipet - 5 mL (1)
Pipet - 10 mL (7)
Culture tube with teflon-lined screw caps, 16 mm x 150 mm (6)
GC autosampler vials with teflon inserts (10)
Centrifuge
Aluminum foil
Refrigerator
10 μL Hamilton syringe (1)

d. Chemicals:

TNT "SARM" - PA 360, Lot #268
Benzene, certified (Fisher Scientific)
Methanol, certified (Fisher Scientific)
Standard Water - distilled water containing 100 mg/L each of sulfate and chloride.

4. Standards

A concentrated stock solution of TNT is prepared by weighing out the following amount of SARM material into a volumetric flask and bringing to volume with methanol.

33.5 mg in 100 mL = 335 mg/L (I)

Dilute stock solutions are prepared in methanol according to the following scheme:

0.2 mL of I to 100 mL = 670 μg/L (II)
10 mL of II to 100 mL = 67 μg/L (III)

The volumetric flasks are wrapped in aluminum foil and stored in the refrigerator until needed. Storage time should not exceed two months.

a. Calibration Standards: Calibration standards are prepared from from the dilute stock solutions by dilution with benzene according to the following scheme:

2 mL of II to 10 mL	=	134 µg/L (A)
1 mL of II to 10 mL	=	67 µg/L (B)
2 mL of III to 10 mL	=	13.4 µg/L (C)
0.5 mL of III to 10 mL	=	3.35 µg/L (D)

b. Control Spikes: Control spikes are prepared by diluting the dilute stock solution with standard water according to the following scheme:

0.5 mL of III to 100 mL	=	0.34 µg/L (A)
1.0 mL of III to 100 mL	=	0.67 µg/L (B)
2.0 mL of III to 100 mL	=	1.34 µg/L (C)
0.5 mL of II to 100 mL	=	3.35 µg/L (D)
1.0 mL of II to 100 mL	=	6.70 µg/L (E)

5. Procedure

Pipet 15 mL of water sample into a new centrifuge tube. Pipet 0.5 mL of benzene into the tube. Screw on the cap and shake well. Centrifuge the tube for 2 minutes. With a micropipet, carefully remove the benzene layer and place it directly into a GC autosampler vial. Add a second 0.5 mL aliquot of benzene to the water sample. Shake and centrifuge. Remove the benzene layer and combine with the first extract in the GC autosampler vial.

The samples are ready for analysis.

Inject 2 µL of the extract onto the GC column in duplicate.

Run standards singly at the beginning and end of each run.

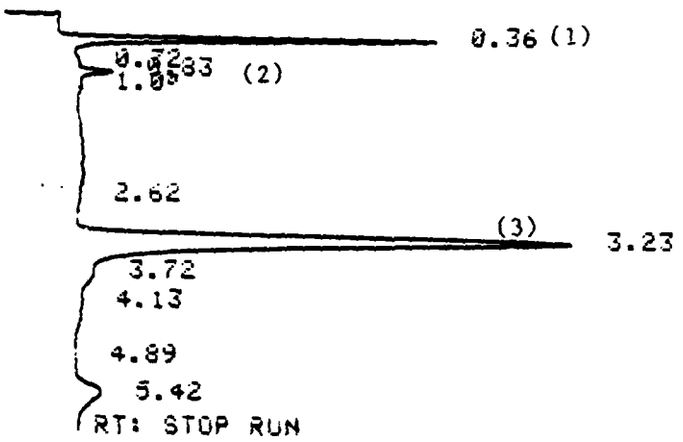
A sample of the TNT peak is presented in Figure B-2.

6. Calculations

A linear regression equation is generated from the peak area versus TNT concentrations of the standards (Equations 1 and 2).

$$\text{slope} = b_1 = \frac{\Sigma x_i y_i - \frac{(\Sigma x_i)(\Sigma y_i)}{n}}{\Sigma x_i^2 - \frac{(\Sigma x_i)^2}{n}} \qquad \text{(Eq. 1)}$$

$$\text{intercept} = b_o = \frac{\Sigma y - b_1(\Sigma x)}{n} \qquad \text{(Eq. 2)}$$



PEAKS

1 - Solvent Benzene
2 - Impurity
3 - TNT - 71 µg/L

Retention Time - TNT 3.23 min.

Instrumentation - Gas Chromatograph - Hewlett-Packard 5880A with Computer Controller and Integrator
Auto Injector
Electron Capture Detector

Column - 1.5% SP-2250/1.95% SP-2401 on 100/120 Supelcoport packed in a 2 mm I.D., 0.25 in. O.D. by 6 ft. glass column

Temperature - injection port - 210°C
oven - 180°C isothermal
detector - 300°C

Carrier Gas: N_2 @ 28 cc/min.

Injection Volume - 2 µL

Figure B-2. Chromatograph of TNT

The duplicate injections of a given detection limit spike are averaged and the found TNT concentration is calculated from Equation 3. These calculations were performed on the data for each of the four days. The raw data and calculations are presented in Tables B11-15. The found versus target TNT concentrations for the four days were evaluated for the TNT detection limit by the Hubaux and Vos (1975) formulae.

$$\frac{\left[\frac{PA_1 + PA_2}{2} \quad b_1\right] + b_o}{16.67*} = \text{found concentration} \qquad \text{(Eq. 3)}$$

PA = peak area
* = concentration factor

In addition, the data were analyzed for standard deviation (Equation 4), percent imprecision (Equation 5), and percent inaccuracy (Equation 6).

$$\text{standard deviation} = s = \left[\frac{n\Sigma x^2 - (\Sigma x)^2}{n(n-1)}\right]^{1/2} \qquad \text{(Eq. 4)}$$

$$\text{percent imprecision} = s/\bar{x} \times 100 \qquad \text{(Eq. 5)}$$

$$\text{percent inaccuracy} = \frac{\bar{x} - \text{ppb added}}{\text{ppb added}} \times 100 \qquad \text{(Eq. 6)}$$

TABLE B-11. TNT

Day 1 Data

Standards			Peak Area of Spiked Samples				
Concentration µg/L	Peak Area		Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
	Inject. 1/Inject. 2						
	9,987	5,191	1986	3485	16.67	0.00	0
3.35	8,899	8,086	5076	5515	16.67	0.54	0.34
13.4	28,707	24,778	6739	8150	16.67	0.91	0.67
67.0	46,840	48,455	10155	14821	16.67	1.79	1.34
134.0			22422	22950	16.67	3.57	3.35
			41643	46478	16.67	7.29	6.70

TABLE B-12. TNT

Day 2 Data

Standards			Peak Area of Spiked Samples				
Concentration µg/L	Peak Area		Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
	Inject. 1/Inject. 2						
	0	0	789	4295	16.67	0.0	0
3.35	1,882	4,024	9092	22147	16.67	0.98	0.34
13.4	7,109	12,128	10343	15001	16.67	0.77	0.67
67.0	49,700	62,332	16202	47036	16.67	2.15	1.34
134.0	98,485	117,950	44500	51529	16.67	3.41	3.35
			87708	103157	16.67	6.96	6.70

TABLE B-13. TNT

Day 3 Data

Standards			Peak Area of Spiked Samples				
Concentration µg/L	Peak Area		Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
	Inject. 1/Inject. 2						
	0	0	1761	4652	16.67	0.00	0
3.35	3,000	3,124	7062	6627	16.67	0.34	0.34
13.4	17,486	21,715	9765	12244	16.67	0.77	0.67
67.0	53,998	66,184	17940	21278	16.67	1.29	1.34
134.0	111,090	121,090	50864	62889	16.67	4.07	3.35
			92559	118348	16.67	7.69	6.70

TABLE B-14. TNT

Day 4 Data

Standards			Peak Area of Spiked Samples				
Concentration µg/L		Peak Area	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
	Inject. 1/Inject. 2						
	0	0	3580	2067	16.67	0.00	0
3.35	2,904	3,438	8586	10538	16.67	0.54	0.34
13.4	17,348	20,180	10674	15302	16.67	0.79	0.67
67.0	55,696	61,308	18202	28144	16.67	1.55	1.34
134.0	106,120	102,552	44434	54604	16.67	3.52	3.35
			88990	105677	16.67	7.10	6.70

TABLE B-15. TNT

Data Summary

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	0	0	0	0	0			
0.335	0.54	0.98	0.34	0.54	0.60	0.27	45.0	78.3
0.67	0.91	0.77	0.77	0.79	0.78	0.11	14.2	16.3
1.34	1.79	2.15	1.29	1.55	1.69	0.37	21.6	26.4
3.35	3.57	3.41	4.07	3.52	3.64	0.29	8.0	8.8
6.7	7.29	6.96	7.69	7.10	7.26	0.32	4.4	8.3

Y = 1.0650 X + 0.1307

Y = TNT concentration in µg/L

X = peak area units

Correlation coefficinet = 0.9952

Detection limit = 0.85 µg/L

C. Analysis of Low Levels of Tetryl in Water - Quantitative
USATHAMA Approval Number 1A

1. Application

The method is used to determine to the quantitative analysis of low levels of tetryl in water using the gas chromatograph.

a. Tested Concentration Range: (µg/L)

Tetryl 2.50 to 50.0 µg/L

b. Sensitivity:

Tetryl - 1310 area units/ng at the detection limit

c. Detection Limits: (µg/L)

Tetryl - 5.3 µg/L

d. Interferences: Glassware must be carefully cleaned; otherwise interferences are observed in the region where tetryl appears on the chromatograms.

e. Analysis Rate: Extraction requires about 75 minutes per sample. GC analysis requires 9 minutes per sample. One analyst can analyze 12 - 18 samples per 8-hour day using 6 magnetic stirrers and a GC autoinjector.

2. Chemistry

$C_7H_5N_5O_8$ Tetryl; Aniline, N-methyl-N-2,4,6-tetranitro-
CAS RN 479-45-8
Melting Point: 131°C
Boiling Point: 187°C (explodes)

Hazards. Use caution in handling tetryl; explosive hazard and toxic hazards exist.

3. Apparatus

a. Instrumentation:

Gas Chromatograph - Varian 3700 with electron capture detector, auto injector, computer controller and integrator.

b. Parameters:

Column - 1.5% SP-2250/1.95% SP-2401 on 100/120 Supelcoport packed in a 2 mm I.D., 0.25 in O.D. by 6 ft. column
Gas Flow - Nitrogen @ 55 ml/min at the detector
Temperature - injection port - 210°C
oven - 180 - 230°C
detector - 330°C
Temperature Programming - 10°C/min.
Injection Volume - 5.5 µL
Detector - electron capture ^{63}Ni
Retention Time - tetryl - 4.64 min.

c. Hardware/Glassware:

Volumetric Flasks - 110 mL with graduated top (6)
Volumetric Flasks - 100 mL (12)
Volumetric Flasks - 10 mL (2)
Pipet - 1 mL (7)
Pipet - 2 mL (1)
Pipet - 5 mL (1)
Pipet - 10 mL (2)
Magnetic Stirrer (6 - one for each sample)
Magnetic Stirring Bars (6 - one for each sample)
GC autosampler vials - teflon septum (10 - one for each sample and standard)
Micropipet
10 µL Hamilton Syringe (1)
Aluminum foil
Refrigerator
Micropipets (6)

d. Chemicals:

Tetryl "SARM" - PA 608, Lot #2714
Benzene, certified (Fisher Scientific)
Methanol, certified (Fisher Scientific)
Sodium Dichromate, ACS grade (Fisher Scientific)
Sulfuric Acid, ACS grade (Fisher Scientific)
Standard Water - distilled water containing 100 mg/L each of sulfate and chloride
Acetone, certified (Fisher Scientific)

4. Standards

Concentrated stock solutions of tetryl are prepared by weighing out the following amount of SARM material into a volumetric flask and bringing to volume with methanol.

50.0 mg tetryl in 100 mL = 500 mg/L (I)
28.2 mg tetryl in 100 mL = 282 mg/L (II)

Dilute stock solutions are prepared by diluting the concentrated stock with methanol according to the following scheme:

1 mL of I to 100 mL = 5 mg/L (III)
10 mL of III to 100 mL = 0.5 mg/L (IV)

The volumetric flasks are wrapped in aluminum foil and stored in a refrigerator until needed. Storage time should not exceed 2 weeks.

a. Calibration:

Working standards are prepared by diluting the stock solution with methanol according to the following scheme:

1 mL of II to 100 mL	= 2820 µg/L
Stock Solution IV	= 500 µg/L
10 mL of A to 100 mL	= 282 µg/L
5 mL of C to 10 mL	= 141 µg/L
1 mL of B to 10 mL	= 50 µg/L

b. Control Spikes:

Blank
0.5 mL of IV to 100 mL = 2.5 µg/L
1.0 mL of IV to 100 mL = 5.0 µg/L
2.0 mL of IV to 100 mL = 10.0 µg/L
0.5 mL of III to 100 mL = 25.0 µg/L
1.0 mL of III to 100 mL = 50.0 µg/L

5. Procedure

Wash all volumetric flasks according to the following sequence: 1) rinse twice with acetone; 2) rinse twice with distilled water; 3) soak for 1 hour in chromic acid; 4) rinse acid from flasks; 5) rinse 3 times with distilled water and 6) dry.

Pour 100 mL of the water sample to be tested in a volumetric with graduated top. Add 1 mL of benzene and a magnetic stirring bar. Place flask on a magnetic stirrer and carefully increase stirring velocity until a good vortex is formed and the solution is well mixed. Continue stirring for 30 minutes. After stirring is completed, allow the benzene to rise to the neck of the volumetric. Measure the benzene layer and carefully draw off the benzene with a micropipet. Place the benzene extract in a GC autosampler vial. Repeat the entire extraction with a second mL of benzene and measure the extract. Combine the second extract with the first extract in the GC autosampler vial. (Total volume is 1.6 mL).

Samples are ready for GC analysis.

Inject 5.5 μL of sample extract into GC column in duplicate and record peak area.

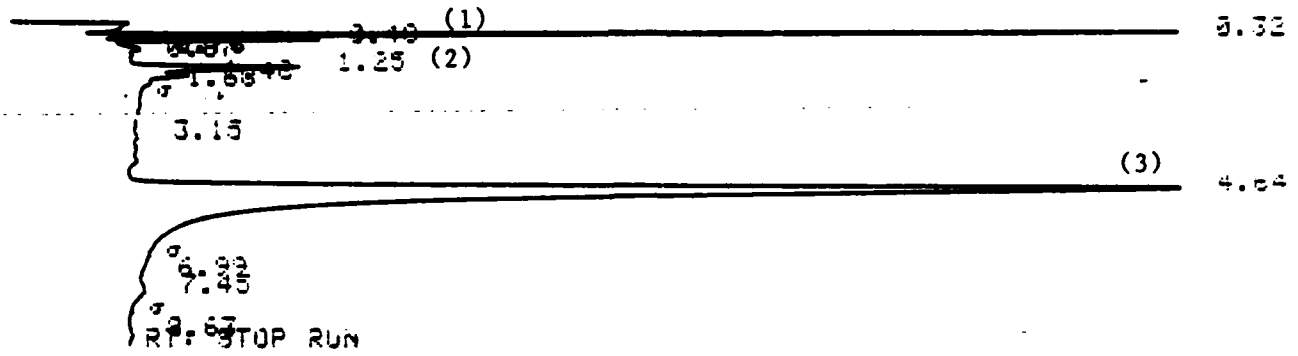
Calibration. Inject working calibration solutions singly at beginning and conclusion of each analytical run. Plot peak area versus ppb of each standard to obtain a working curve. A sample of the tetryl peak is presented in Figure B-3.

6. Calculations

A linear regression equation is generated from the peak heights versus tetryl concentrations of the standards (Equations 1 and 2).

$$\text{slope} = b_1 = \frac{\Sigma x_i y_i - \frac{(\Sigma x_i)(\Sigma y_i)}{n}}{\Sigma x_i^2 - \frac{(\Sigma x_i)^2}{n}} \qquad \text{(Eq. 1)}$$

$$\text{intercept} = b_o = \frac{\Sigma y - b_1(\Sigma x)}{n} \qquad \text{(Eq. 2)}$$



PEAKS

1 - Solvent Benzene
2 - Impurity
3 - Tetryl - 331.2 µg/L

Retention Time - Tetryl = 4.64 min.

Instrumentation - Gas Chromatograph - Hewlett-Packard 5880A with Computer Controller and Integrator
Auto Injector
Electron Capture Detector

Column - 1.5% SP-2250/1.95% SP-2401 on 100/120 Supelcoport packed in a 2 mm I.D., 0.25 in. O.D. by 6 ft. glass column

Temperature - Injection port - 210°C
Oven - 180-230°C
Detector - 330°C

Temperature Programming - 10°C/min.

Injection Volume - 5.5 µL

Carrier Gas - N_2 @ 55 mL/min.

Figure B-3. Chromatograph of Tetryl

The duplicate injections of a given detection limit spike are averaged and the found tetryl concentration is calculated from Equation 3. These calculations were performed on the data for each of the four days. The raw data and calculations are presented in Tables B16-20. The found versus target tetryl concentrations for the four days were evaluated for the tetryl detection limit by the Hubaux and Vos (1975) formulae.

$$\frac{\left[\frac{PA_1 + PA_2}{2} \quad b_1\right] + b_o}{62.5^*} = \text{found concentration} \qquad \text{(Eq. 3)}$$

PA = peak height
* = concentration factor

In addition, the data were analyzed for standard deviation (Equation 4), percent imprecision (Equation 5), and percent inaccuracy (Equation 6).

$$\text{standard deviation} = s = \left[\frac{n\Sigma x^2 - (\Sigma x)^2}{n(n-1)}\right]^{1/2} \qquad \text{(Eq. 4)}$$

$$\text{percent imprecision} = s/\bar{x} \times 100 \qquad \text{(Eq. 5)}$$

$$\text{percent inaccuracy} = \frac{\bar{x} - \text{ppb added}}{\text{ppb added}} \times 100 \qquad \text{(Eq. 6)}$$

TABLE B-16. Tetryl

Day 1 Data

Standards		Peak Area of Spiked Samples				
Concentration µg/L	Peak Area	Injection 1	Injection 2	Concentration Factor	Found Concentration µg/L	Target Concentration µg/L
50	197	0	0	62.5	0	0
141	1145	1354	1376	62.5	2.54	2.5
282	2940	3917	3694	62.5	4.53	5.0
500	11307	9149	10493	62.5	7.26	10.0
2820	108250	60812	61275	62.5	31.71	25.0
		105822	105294	62.5	44.41	50.00

TABLE B-17. Tetryl

Day 2 Data

Standards		Peak Area of Spiked Samples				
Concentration µg/L	Peak Area	Injection 1	Injection 2	Concentration Factor	Found Concentration µg/L	Target Concentration µg/L
50	201	0	0	62.5	0	0
141	886	932	651	62.5	1.78	2.5
282	5076	3910	3415	62.5	5.03	5.0
500	10946	13597	8943	62.5	7.92	10.0
2820	122360	66371	66936	62.5	30.25	25.0
		119760	128097	62.5	39.03	50.0

TABLE B-18. Tetryl

Day 3 Data

Standards		Peak Area Spiked Samples				
Concentration µg/L	Peak Area	Injection 1	Injection 2	Concentration Factor	Found Concentration µg/L	Target Concentration µg/L
50	71	0	0	62.5	0	0
141	-	1802	1620	62.5	2.32	2.5
282	3303	4914	4861	62.5	4.66	5.0
500	11564	9812	10094	62.5	7.32	10.0
2820	115235	69156	68752	62.5	31.59	25.0
		119285	123553	62.5	55.85	50.0

TABLE B-19. Tetryl

Day 4 Data

Standards		Peak Area of Spiked Samples				
Concentration µg/L	Peak Area	Injection 1	Injection 2	Concentration Factor	Found Concentration µg/L	Target Concentration µg/L
50	383	0	0	62.5	0	0
141	1107	1085	1099	62.5	2.82	2.5
282	3814	3885	4316	62.5	4.42	5.0
500	11440	12285	15244	62.5	8.90	10.0
2820	118318	74819	70019	62.5	29.36	25.0
		120760	129097	62.5	57.77	50.0

TABLE B-20. Tetryl Detection Limit

Data Summary

Target Concentration (µg/L)	Found Concentration µg/L Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	0	0	0	0	0			
2.5	2.54	1.78	2.32	2.82	2.37	0.44	18.6	-5.4
5.0	4.53	5.03	4.66	4.42	4.66	0.27	5.7	-6.8
10.0	7.26	7.92	7.32	8.90	7.85	0.76	9.7	-21.5
25.0	31.71	30.25	31.59	29.36	30.73	1.13	3.7	22.9

Y = 1.2361 X - 1.3868

Y = Tetryl concentration in µg/L

X = Peak area

Correlation coefficient = 0.9876

Detection limit = 5.3 µg/L

D. Analysis of Low Levels of Nitroglycerine and PETN in Water - Quantitative
USATHAMA Approval Number 6B

1. Application

Method used to determine the concentration of nitroglycerine and PETN in water.

a. Tested Concentration Range: (µg/L)

Nitroglycerine - 5.29 to 52.9 µg/L
PETN - 5.40 to 54.0 µg/L

b. Sensitivity:

Nitroglycerine - 0.108 mm/ng based on a 23.1 ng injection
PETN - 0.16 mm/ng based on a 18.7 ng injection

c. Detection Limits: (µg/L)

Nitroglycerine - 8.1 µg/L
PETN - 10.3 µg/L

d. Interferences: None observed.

e. Analysis Rate: A set of 6 samples can be extracted, dried, and diluted in about 3 hours. LC analysis requires 10 minutes per sample.

2. Chemistry

$C_3H_5N_3O_9$	Nitroglycerine, 1,2,3-propanetriol trinitrate
CAS RN	55-63-0
M.W.	227.09
	Explodes at 218°C

Toxic effects by ingestion, inhalation, and absorption through the skin range from headaches and rashes to vomiting, delirium, paralysis and death.

$C_5H_8N_4O_{12}$	PETN, Pentaerythritol Tetranitrate, 2,2-bis[(nitrooxy)-methyl]-1,3-propanediol dinitrate (ester)
CAS RN	78-11-5
M.W.	316.15
Melting Point:	140°C

Extreme caution must be observed in the handling of PETN, as it explodes upon percussion.

3. Apparatus

a. Instrumentation:

HPLC - Perkin-Elmer 601 LC with LC55 variable wavelength UV spectrophotometer detector at a wavelength of 204 nm, and a LC420 autosampling system.

b. Parameters:

Column - Waters radial compression column (10 cm x 7 mm I.D.), 10 micron silica
Carrier Solvent - 2.5% isopropanol/97.5% hexane
Flow Rate - 2 ml/min.
Retention Time = PETN 4.65 min
NG 6.32 min

c. Hardware/Glassware:

Volumetric Flasks - 100 mL (6)
Volumetric Flasks - 1000 mL (3)
Culture tubes (20 mL) with teflon-lined screw caps (52)
Graduated Cylinder - 100 mL (1)
Separatory Funnel - 250 mL (1)
Disposable Pipets - 1 mL (38)
Disposable Pipets - 5 mL (4)
Pasteur Pipets (52)
Silli Evaporator
Autosampler Vials - teflon septum (52)
Refrigerator

d. Chemicals:

Nitroglycerine "SARM" (Battelle I.D. #PA596)
PETN "SARM" (Battelle I.D. #PA604)
Isopropanol, HPLC grade (Fisher Scientific)
Standard Water - distilled water containing 100 mg/L each of sulfate and chloride
Methylene Chloride, HPLC grade (Fisher Scientific)
N-Hexane, HPLC grade (JT Baker)
Acetonitrile, HPLC grade (JT Baker)
Nitrogen Gas, regular (Air Products)

4. Standards

Concentrated stock solutions are made by dissolving SARM material in acetonitrile and diluting to final volume with isopropanol.

105.66 mg nitroglycerine in 100 mL = 1056.6 mg/L (I)
83.5 mg PETN in 100 mL = 855 mg/L (II)

Dilute stock solutions are prepared by diluting the concentrated stock solutions with isopropanol according to the following scheme:

1 mL of I to 100 mL = 10.57 mg/L (III)
1 mL of II to 100 mL= 8.55 mg/L (IV)

These volumetric flasks are wrapped in aluminum foil and stored in a refrigerator.

A stock solution for preparing spikes is made daily by diluting with standard water as follows:

2 mL of III + 2.5 mL of IV to 20 mL (V)	= NG	1.06	mg/L
	= PETN	1.07	mg/L

A stock solution for preparing calibration standards is made daily, diluting with isopropanol as follows:

1 mL of I + 1 mL of II to 20 mL (VI)	= NG	52.8	mg/L
	= PETN	42.8	mg/L

a. Calibration: Working standards are prepared by diluting the stock solutions with hexane according to the following scheme:

1 mL of VI to 8 mL	= NG	6.6	mg/L	(VII)
	PETN	5.3	mg/L	
1 mL of VI to 10 mL	= NG	5.28	mg/L	(VIII)
	PETN	4.28	mg/L	
1 mL of VI to 20 mL	= NG	2.64	mg/L	(IX)
	PETN	2.14	mg/L	
0.5 mL of VI to 20 mL	= NG	1.32	mg/L	(X)
	PETN	1.07	mg/L	
1 mL of VIII to 10 mL	= NG	528	µg/L	(XI)
	PETN	428	µg/L	
1 mL of IX to 10 mL	= NG	264	µg/L	(XII)
	PETN	214	µg/L	
1 mL of X to 10 mL	= NG	132	µg/L	(XIII)
	PETN	107.1	µg/L	

b. Control Spikes: Control spikes are prepared by diluting stock solutions with standard water as follows:

Blank (1)

0.5 mL of V to 100 mL	=	NG	5.3 µg/L	(2)
		PETN	5.4 µg/L	
1.0 mL of V to 100 mL	=	NG	10.6 µg/L	(3)
		PETN	10.7 µg/L	
2.0 mL of V to 100 mL	=	NG	21.2 µg/L	(4)
		PETN	21.4 µg/L	
5.0 mL of V to 100 mL	=	NG	53.0 µg/L	(5)
		PETN	54.0 µg/L	
10.0 mL of V to 100 mL	=	NG	106.0 µg/L	(6)
		PETN	107.0 µg/L	

One set of control spikes are prepared and tested on four consecutive days.

5. Procedure

Pour 100 mL sample to be tested into a 250 mL separatory funnel and add 4 mL of methylene chloride. Swirl at least one minute and allow to separate. Draw out extract with a pasteur pipet and place into a 20 mL screw capped tube. Repeat procedure with another 4 mL of methylene chloride and combine the extracts. Blow dry the extract under a stream of nitrogen. Add 2 mL of hexane to the sample and shake to insure that all of the sample is dissolved. Transfer contents to an autosampler vial. Sample is ready for LC analysis.

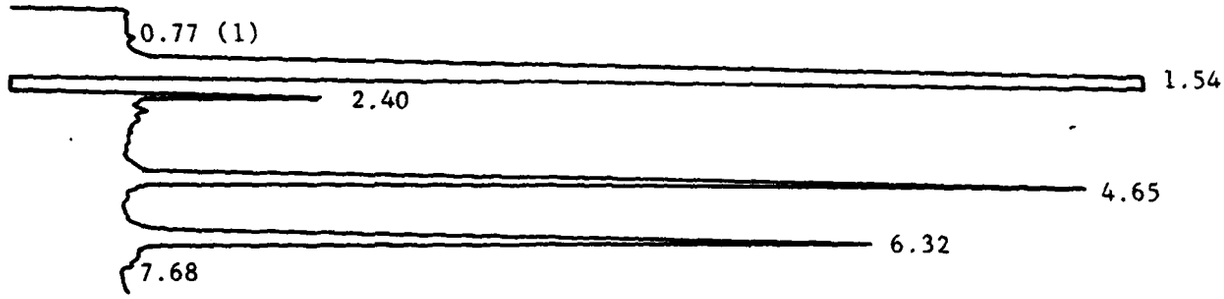
Samples are injected into the HPLC by autosampler with a 175 µL loop. A sample NG and PETN spectrum is presented in Figure B-4.

6. Calculations

A linear regression equation is generated from the peak heights versus nitroglycerine or PETN concentrations of the standards (Equations 1 and 2).

$$\text{slope} = b_1 = \frac{\Sigma x_i y_i - \frac{(\Sigma x_i)(\Sigma y_i)}{n}}{\Sigma x_i^2 - \frac{(\Sigma x_i)^2}{n}} \qquad \text{(Eq. 1)}$$

$$\text{intercept} = b_o = \frac{\Sigma y - b_1(\Sigma x)}{n} \qquad \text{(Eq. 2)}$$



PEAKS

1 - Solvent Benzene
2 - PETN 2.14 mg/L
3 - Nitroglycerine - 2.64 mg/L

Retention Time - PETN = 4.65 min.
Nitroglycerine= 6.32 min.

Instrumentation - Perkin-Elmer #601 LC with LC55 Variable Wavelength UV Spectrophotometer Detector and LC420 Autosampler

Column - Waters Radial Compression Column (10 cm x 7 mm I.D.) 10 micron silicon

Carrier Solvent - 2.5% isopropanol/97.5% hexane

Flow Rate - 2 mL/min.

Detector - 201 nm

Injection Volume - 175 µL

Figure B-4. Chromatograph of PETN and Nitroglycerine

The duplicate injections of a given detection limit spike are averaged and the found nitroglycerine or PETN concentrations are calculated from Equation 3. These calculations were performed on the data for each of the four days.

$$\frac{\left[\frac{PH_1 + PH_2}{2} \quad b_1\right] + b_o}{50^*} = \text{found concentration} \qquad \text{(Eq. 3)}$$

PH = peak height
* = concentration factor

The raw data and calculations for nitroglycerine and PETN are presented in Tables B21 - 30. The found versus target concentrations for the four days were evaluated for their detection limit by the Hubaux and Vos (1975) formulae. In addition, the data were analyzed for standard deviation (Equation 4), percent imprecision (Equation 5), and percent inaccuracy (Equation 6). The detection limits for nitroglycerine and PETN were 8.1 µg/L and 10.3 µg/L, respectively.

$$\text{standard deviation} = s = \left[\frac{n\Sigma x^2 - (\Sigma x)^2}{n(n-1)}\right]^{1/2} \qquad \text{(Eq. 4)}$$

$$\text{percent imprecision} = s/\bar{x} \times 100 \qquad \text{(Eq. 5)}$$

$$\text{percent inaccuracy} = \frac{\bar{x} - \text{ppb added}}{\text{ppb added}} \times 100 \qquad \text{(Eq. 6)}$$

TABLE B-21. Nitroglycerine

Day 1 Data

Standards		Peak Height of Spiked Samples				
Concentration mg/L	Peak Ht. cm	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	0	0	50	0	0
0.132	0.2	0.1	0.15	50	1.4	5.3
0.264	0.45	0.5	0.4	50	6.2	10.6
0.528	1.0	1.3	1.0	50	16.4	21.2
1.32	2.0	3.2	2.9	50	43.6	53.0
2.64	3.9					
5.28	7.4					

TABLE B-22. Nitroglycerine

Day 2 Data

Standards		Peak Height of Spiked Samples				
Concentration mg/L	Peak Ht. cm	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	0	0	50	0	0
0.132	0.2	0.35	0.35	50	3.2	5.3
0.264	0.5	0.6	0.6	50	6.4	10.6
0.528	1.1	1.1	1.1	50	12.8	21.2
1.32	-	3.3	3.2	50	41.0	53.0
2.64	4.3					
5.28	7.8					

TABLE B-23. Nitroglycerine

Day 3 Data

Standards		Peak Height of Spiked Samples				
Concentration mg/L	Peak Ht. cm	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	0	0	50	0	0
0.132	0.25	0.25	0.3	50	2.5	5.3
0.264	0.45	0.55	0.6	50	6.0	10.6
0.528	1.05	1.3	1.4	50	16.0	21.2
1.32	2.2	3.65	3.45	50	44.0	53.0
2.64	4.2					
5.28	8.05					
6.6	9.75					

TABLE B-24. Nitroglycerine

Day 4 Data

Standards		Peak Height of Spiked Samples				
Concentration mg/L	Peak Ht. cm	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	0	0	50	0	0
0.132	0.25	0.1	0.05	50	0	5.3
0.264	0.45	0.6	0.55	50	6.0	10.6
0.528	1.10	1.25	1.2	50	14.4	21.2
1.32	2.2	3.8	3.85	50	47.6	53.0
2.64	4.2					
5.28	8.1					

TABLE B-25. Nitroglycerine

Data Summary

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Inaccuracy	Percent Imprecision
0	0	0	0	0	0	0	0	0
5.3	1.4	3.2	2.5	0.0	1.78	1.40	-66.5	78.7
10.6	6.2	6.4	6.0	6.6	6.15	0.19	-42.0	3.1
21.2	16.4	12.8	16.0	14.4	14.9	1.65	-29.7	11.0
53.0	43.0	41.0	44.0	47.6	44.1	2.71	-16.9	6.2

$Y = 0.8563 X - 2.0562$

Y = nitroglycerine levels in µg/L

X = peak height in cm

Correlation coefficient = 0.9937

Detection limit = 8.1 µg/L

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EVALUATION OF SOLID SORBENTS FOR SAMPLING AND ANALYSIS OF EXPLO--ETC(U
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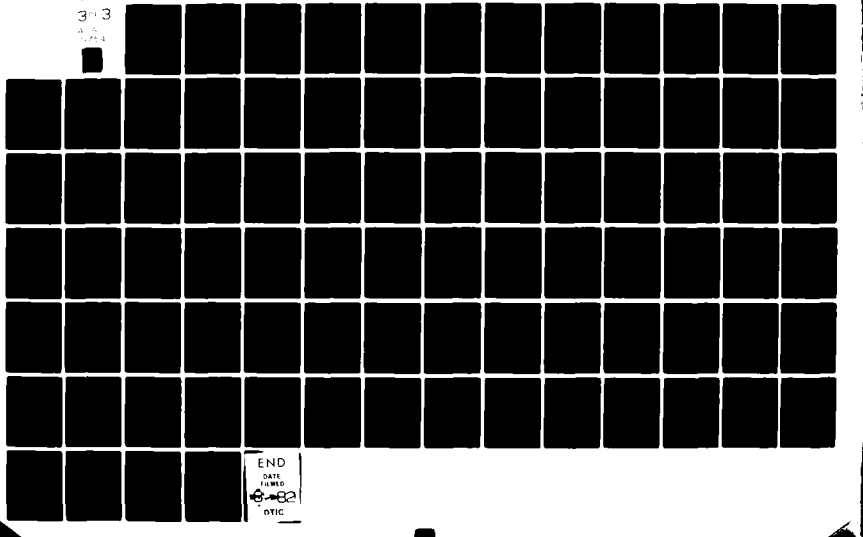

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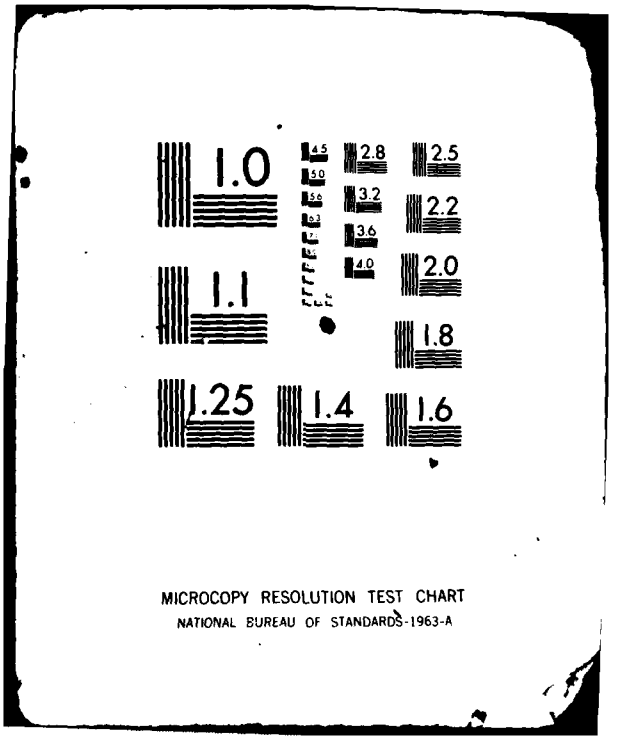
1.0
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4.5
5.0
5.6
6.3
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

TABLE B-26. PETN

Day 1 Data

Standards		Peak Height of Spiked Samples				
Concentration mg/L	Peak Ht. cm	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	0	0	50	0	0
0.107	0.3	0.3	0.3	50	3.7	5.4
0.214	0.6	1.0	0.8	50	11.2	10.7
0.428	1.3	2.3	1.8	50	25.4	21.4
1.07	2.6	4.5	4.5	50	55.7	54.0
2.14	5.1					
4.28	8.7					

TABLE B-27. PETN

Day 2 Data

Standards		Peak Height of Spiked Samples				
Concentration mg/L	Peak Ht. cm	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	0	0	50	0	0
0.107	0.3	0.7	0.7	50	4.8	5.4
0.214	0.7	1.3	1.3	50	10.3	10.7
0.428	1.4	2.3	2.2	50	19.1	21.4
2.14	5.5	5.25	5.1	50	46.1	54.0

TABLE B-28. PETN

Day 3 Data

Standards		Peak Height of Spiked Samples				
Concentration mg/L	Peak Ht. cm	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	0	0	50	0	0
0.107	0.3	0.7	0.7	50	4.8	5.4
0.214	0.65	1.25	1.3	50	9.6	10.7
0.428	1.4	2.25	2.3	50	24.9	21.4
1.07	2.5	5.3	5.2	50	48.4	54.0
2.14	5.45					
4.28	9.15					

TABLE B-29. PETN

Day 4 Data

Standards		Peak Height of Spiked Samples				
Concentration mg/L	Peak Ht. cm	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	0	0	50	0	0
0.107	0.3	0.8	0.8	50	5.7	5.4
0.214	0.6	1.25	1.2	50	9.6	10.7
0.428	1.4	2.6	2.55	50	22.1	21.4
1.07	2.8	6.4	6.4	50	57.3	54.0
2.14	5.2					
4.28	9.3					

TABLE B-30. PETN

Data Summary

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	0	0	0	0	0			
5.4	3.7	4.8	4.8	5.7	4.75	0.82	17.2	-12.0
10.7	11.2	10.3	9.0	9.6	10.03	0.95	9.4	- 6.3
21.4	25.4	19.1	24.9	22.1	22.88	2.91	12.7	6.9
54.0	55.7	46.1	48.4	57.3	51.88	5.46	10.5	- 3.9

Y = 0.9687 + 0.1786

Y = PETN concentration in µg/L

X = peak height in cm

Correlation coefficient = 0.9901

Detection limit = 10.3 µg/L

E. Analysis of Low Levels of RDX in Water - Quantitative
USATHAMA Approval Number 6B

1. Application

The method is applicable to the quantitative analysis of low levels of RDX in water using high performance liquid chromatography.

a. Tested Concentration Range: (µg/L)

4.15 to 82.9 µg/L

b. Sensitivity:

0.432 mm deflection based on an 8.1 ng injection.

c. Detection Limit: (µg/L)

7.5 µg/L

d. Interferences: RDX is subject to photolysis and should be protected from the light.

e. Analysis Rate: Sample extraction requires 10 minutes per sample. HPLC run takes 6 minutes. An analyst can analyze approximately 20 samples per day with 2 hours for column conditioning.

2. Chemistry

$C_3H_6N_6O_6$	Hexahydro-1,3,5-Trinitro-1,3,5-Triazine
CAS RN	121-82-4
Melting Point:	204°C
Boiling Point:	Not available

Hazards. Use caution in handling RDX. Potential explosive and toxic inhalation hazards exist.

3. Apparatus

a. Instrumentation:

HPLC - Perkin-Elmer #601 Liquid Chromatograph with Perkin-Elmer UV spectrophotometer with LC-55 variable wavelength detector, Waters Radial Compression Unit, Cole Parmer Recorder, and LC-420 Autosampler.

b. Parameters:

Column - Waters 10 micron silica normal phase radial compression column
Mobile Phase - isocratic, 55.3% hexane/14.9% acetonitrile/29.8% methylene chloride @ 1.5 mL/min.
Detector - 232 nm
Injection Volume - 175 µL
Retention Time - 5.6 min.

c. Hardware/Glassware:

Volumetric Flasks - 100 mL (4)
Volumetric Flasks - 25 mL (1)
Volumetric Flasks - 10 mL (4)
Pipet - 25 mL (1)
Pipet - 10 mL (2)
Pipet - 5 mL (2)
Pipet - 1 mL (6)
Graduated Cylinder - 100 mL (1)
Beaker - 250 mL (1)
Separatory Funnel - 125 mL (6)
Culture Tubes - 10 mL with teflon-lined screw caps (6)
Pasteur pipets
Aluminum foil
Refrigerator

d. Chemicals:

RDX "SARM" - Lot #HOL475-1, PA 361 and PA 534
Hexane - HPLC Baker analyzed reagent
Methylene Chloride - HPLC Baker analyzed reagent
Acetonitrile - HPLC Baker analyzed reagent
Methanol - HPLC Baker analyzed reagent
Standard Water - distilled water containing 100 mg/L of each sulfate and chloride.
Distilled Water

7. Standards

Concentrated stock solution of RDX is prepared by weighing out 27.75 mg of SARM material into a 100 mL volumetric flask and bringing to volume with methanol (277.5 mg/L) (I). This volumetric is wrapped in aluminum foil and stored in a refrigerator until needed. Storage time should not exceed one month.

a. Calibration Standards:

Working standards are prepared by diluting the concentrated stock solution according to the following scheme with methylene chloride:

1 mL of I to 10 mL = 27.75 mg/L (II)
1 mL of I to 20 mL = 13.88 mg/L (III)
0.5 mL of I to 20 mL = 6.94 mg/L (IV)

1 mL of II to 10 mL = 2.78 mg/L (A)
1 mL of II to 15 mL = 1.85 mg/L (B)
1 mL of III to 10 mL = 1.39 mg/L (C)
1 mL of IV to 10 mL = 694 µg/L (D)
1 mL of A to 10 mL = 278 µg/L (E)
1 mL of C to 10 mL = 139 µg/L (F)
1 mL of C to 15 mL = 92.7 µg/L (G)
1 mL of D to 10 mL = 69.4 µg/L (H)
1 mL of D to 15 mL = 46.2 µg/L (J)

Standards are run daily using 175 µL injections.

b. Control Spikes: Concentrated stock solution of RDX SARM is prepared by weighing out 24.93 mg into a 25 mL volumetric flask and bringing up to volume with methanol (1037.2 mg/L) (I).

The following dilutions are prepared in methanol and standard water by the following scheme:

1 mL of I to 100 mL = 10.37 mg/L (II)
1 mL of II to 10 mL = 1.037 mg/L (III)

Control spike samples are made up in "standard water" according to the following scheme:

Blank
0.5 DL - 0.4 mL of III to 100 mL = 4.15 µg/L
1.0 DL - 0.8 mL of III to 100 mL = 8.29 µg/L
2.0 DL - 1.6 mL of III to 100 mL = 16.59 µg/L
5.0 DL - 4.0 mL of III to 100 mL = 41.48 µg/L
10.0 DL - 8.0 mL of III to 100 mL = 82.96 µg/L

5. Procedure

One Hundred mL of a control spike solution is placed in a 125 mL separatory funnel. Two mL of methylene chloride are added and the separatory funnel shaken

vigorously. The methylene chloride layer is allowed to separate and be drawn off into a screw cap tube. The extraction procedure is repeated with a second 2 mL portion of methylene chloride and the extracts combined. The extract is transferred to an autosampler vial.

Samples are injected into the HPLC in duplicate by autosampling with a 175 µL loop.

Standards are injected at the beginning and end of each run.

A sample of the RDX chromatogram is presented in Figure B-5.

6. Calcualtions

A linear regression equation is generated from the peak heights versus RDX concentrations of the standards (Equations 1 and 2).

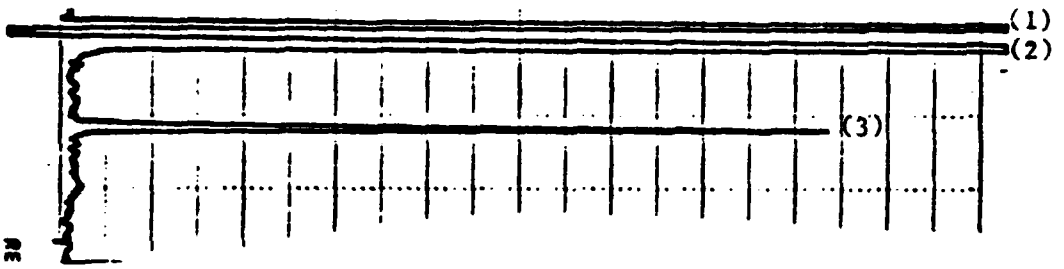
$$\text{slope} = b_1 = \frac{\Sigma x_i y_i - \frac{(\Sigma x_i)(\Sigma y_i)}{n}}{\Sigma x_i^2 - \frac{(\Sigma x_i)^2}{n}} \qquad \text{(Eq. 1)}$$

$$\text{intercept} = b_o = \frac{\Sigma y - b_1(\Sigma x)}{n} \qquad \text{(Eq. 2)}$$

The duplicate injections of a given detection limit spike are averaged and the found concentration is calculated from Equation 3. These calculations were performed on the data for each of the four days. The raw data and calculations are presented in Tables B-31-35. The found versus target RDX concentrations for the four days were evaluated for the RDX detection limit by the Hubaux and Vos (1975) formulae.

$$\frac{\left[\frac{PH_1 + PH_2}{2} \quad b_1\right] + b_o}{25^*} = \text{found concentration} \qquad \text{(Eq. 3)}$$

PH = peak height
* = concentration factor



PEAKS

1 - Solvent Methylene Chloride
2 - Solvent
3 - RDX - 1.39 mg/L

Retention Time - RDX - 5.6 min.

Instrumentation - Perkin-Elmer #601 LC with LC55 Variable Wavelength UV Spectrophotometer Detector and LC420 Autosampler

Column - Waters Radial Compression Column (10 cm x 7 mm I.D.) 10 micron silica

Carrier Solvent - 55.3% hexane/14.9% acetonitrile/29.8% methylene chloride

Flow Rate - 1.5 mL/min.

Detection - 232 nm

Injection - 175 µL

Table B-5. Chromatograph of RDX

In addition, the data were analyzed for standard deviation (Equation 4), percent imprecision (Equation 5), and percent inaccuracy (Equation 6). The detection limit for RDX is 7.5 µg/L.

$$\text{standard deviation} = s = \left[\frac{n\Sigma x^2 - (\Sigma x)^2}{n(n-1)}\right]^{1/2} \qquad \text{(Eq. 4)}$$

$$\text{percent imprecision} = s/\bar{x} \times 100 \qquad \text{(Eq. 5)}$$

$$\text{percent inaccuracy} = \frac{\bar{x} - \text{ppb added}}{\text{ppb added}} \times 100 \qquad \text{(Eq. 6)}$$

TABLE B-31. RDX

Day 1 Data

Standards		Peak Height of Spiked Samples				
Concentration mg/L	Peak Ht. cm	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	0	0	25	0	0
0.0694	0.50	0.35	0.45	25	1.71	4.15
0.092	0.70	1.25	1.25	25	4.89	8.29
0.139	1.05	1.75	1.80	25	10.94	16.59
0.278	2.1	5.35	5.30	25	27.61	41.48
0.694	5.15					
1.39	10.4					

TABLE B-32. RDX

Day 2 Data

Standards		Peak Height of Spiked Samples				
Concentration mg/L	Peak Ht. cm	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	0	0	25	0	0
0.069	0.5	0.4	0.45	25	1.71	4.15
0.092	0.7	0.75	0.70	25	6.65	8.29
0.139	1.05	2.4	1.8	25	10.15	16.59
0.278	2.1	4.4	4.3	25	24.26	41.48
0.694	5.15					
1.39	10.4					

TABLE B-33. RDX

Day 3 Data

Standards		Peak Height of Spiked Samples				
Concentration mg/L	Peak Ht. cm	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	0	0	25	0	0
0.069	0.45	0.35	0.35	25	2.07	4.15
0.092	0.65	0.95	0.9	25	3.74	8.29
0.139	1.1	1.85	1.90	25	11.40	16.59
0.278	2.2	5.0	5.05	25	23.65	41.48
0.694	5.05					
1.39	10.0					

TABLE B-34. RDX

Day 4 Data

Standards		Peak Height of Spiked Samples				
Concentration mg/L	Peak Ht. cm	Injection 1	Injection 2	Concentration Factor	Average Found Concentration µg/L	Target Concentration µg/L
0	0	0	0	25	0	0
0.069	0.45	0.3	0.4	25	1.93	4.15
0.092	0.70	1.3	1.15	25	6.50	8.29
0.139	1.05	2.1	2.0	25	9.57	16.59
0.278	2.2	4.5	4.55	25	29.29	41.48
0.694	5.05					
1.39	10.3					

TABLE B-35. RDX Detection Limig

Data Summary

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percnet Inaccuracy
0	0	0	0	0	0			
4.15	1.71	1.71	2.07	1.93	1.86	0.18	9.5	-55.3
8.28	4.89	6.65	3.74	6.50	5.45	1.39	22.5	-34.3
16.59	10.94	10.15	11.40	9.57	10.52	0.81	7.7	-36.6
41.48	27.61	24.26	23.65	29.29	26.20	2.70	10.3	-36.8

Y = 0.6377 X - 0.1890

Y = RDX concentration in µg/L

X = peak height in cm

Correlation coefficient = 0.9911

Detection limit = 7.5 µg/L

APPENDIX C

Solid Sorbent Methods for Removal and Analysis of Explosives in Water

A. Analysis of Low Levels of RDX, TNT, 2,4-DNT, and 2,6-DNT in Water With the Use of Solid Sorbent Tubes - Quantitative

1. Application

Method used to determine the concentration of RDX, TNT, 2,4-DNT, and 2,6-DNT in water using solid sorbent tubes.

a. Tested Concentration Range: (µg/L)

RDX	-	0.40 to 8.04
TNT	-	0.45 to 9.01
2,4-DNT	-	0.50 to 10.02
2,6-DNT	-	0.48 to 9.51

b. Sensitivity:

RDX	-	0.88 peak height units/ng based on a 15.6 ng injection
TNT	-	19.5 peak height units/pg based on a 35.4 pg injection
2,4-DNT	-	29.2 peak height units/pg based on a 35.4 pg injection
2,6-DNT	-	75.2 peak height units/pg based on a 46.2 pg injection

c. Detection Limits:

RDX	-	0.64 µg/L
TNT	-	1.50 µg/L
2,4-DNT	-	1.69 µg/L
2,6-DNT	-	0.97 µg/L

d. Interferences: Contaminants in sorbents must be removed by soxhlet extraction with acetone before use.

e. Analysis Rate: With two pumps, 8 samples can be collected, run, and analyzed each day.

2. Chemistry

$C_3H_6N_6O_6$ Hexahydro-1,3,5-trinitro-1,3,5-triazine
CAS RN 121-82-4
Melting Point: 204°C
Boiling Point: Not Available

$C_7H_5N_3O_6$ Toluene-2,4,6-trinitro-
CAS RN 118-96-7
Melting Point: 80.75°C
Boiling Point: 240°C (explodes)

$C_7H_6N_2O_4$ Toluene-2,4-dinitro-
CAS RN 121-14-2
Melting Point: 71°C
Boiling Point: 300°C (partially decomposes)

$C_7H_6N_2O_4$ Toluene-2,6-dinitro-
CAS RN 606-20-2
Melting Point: 66°C
Boiling Point: Not Available

Hazards: Use caution in handling these compounds. Explosive and toxic hazards exist.

3. Apparatus

a. Instrumentation:

Gas Chromatograph - Hewlett-Packard 5880A with computer controller and integrator, autoinjector, and electron capture detector.
HPLC - Perkin-Elmer, #LC-601 with Perkin-Elmer #LC-55 variable UV-visible spectrometer
Hewlett-Packard 5880A GC integrator/recorder
Perkin-Elmer #LC-420 Autosampler with rheodyne #7010 automated sampling valve with 200 µl sample loop

b. Parameters:

Gas Chromatograph - Column - 1.5% SP-2250/1.95% SP-2401 on 100/120 supelcoport packed in a 2 mm I.D., 0.25 in O.D. by 6 ft. column
Temperature - Injection Port - 210°C
Oven - 185°C
Detector - 300°C
Carrier Gas - Nitrogen at 28 cc/min
Detector - Electron Capture
Injection Volume - 2 µL
Retention Time - TNT - 3.2 minutes
2,4-DNT - 1.30 minutes
2,6-DNT - 1.70 minutes
Perkin-ELmer HPLC - Column - Waters 10 micron silica column 10 cm x 7 mm Radial Compression Cartridge
Mobile Phase - 61% hexane, 26% methylene chloride, 13% acetonitrile
Flow Rate - 1.5 mL/min
UV Detector @ 232 nm

Before use, solvent is filtered through a 0.45 micron non-aqueous membrane filter using a millipore filtration apparatus. Solvent is then degasses in delivery cylinders using a helium sparger

c. Glassware/Hardware:

Volumetric Flasks - 1000 mL (7)
Volumetric Flasks - 100 mL (17)
Volumetric Flasks - 10 mL (12)
Volumetric Flasks - 5 mL (6)
Beaker - 1000 mL (1)
Pipet, Disposable - 1 mL (40)
Pipet, Disposable - 5 mL (46)
Pipet, Disposable - 10 mL (8)
Flask - 4 liter (2), for mixing LC carrier solvents
Graduated Centrifuge Tubes (24)
GC Autosampler Vials with Teflon Lined Screw Caps
Teflon Sleeves - 5/16 in. I.D. (6)
Slo-Syn Synchronous Stepping Motor FMI-Lab Pump Model #SS50-1296
Teflon Tubing for Pump
Waters Associates - Porapak S Mesh 80/100 #27072
Aluminum Foil
Millipore Filter Apparatus (1)
0.45 micron non-aqueous millipore filters
Gas Sparger (1)
10 µL Hamilton Syringe (1)
Refrigerator
Analytical Balance
Ring Stands (6)
Clamps (6)
Funnel, Glass (1)

d. Chemicals:

RDX "SARM" #475-1/PA534 (Working Standards)
RDX "SARM" #475-1/PA539 (Control Spikes)
TNT "SARM" #268/PA601
2,4-DNT "SARM" #28493-A/PA602
2,6-DNT "SARM" #31640-A/PA603
Methanol - HPLC Certified Grade
Acetone - Fisher Scientific certified
Benzene - Fisher Scientific certified
Methylene Chloride - HPLC Grade
Hexane - HPLC Grade
Acetonitrile - HPLC Grade
Sodium Sulfate, Anhydrous - Fisher Scientific certified
Helium (Purified)
Nitrogen (Purified)
Standard H_2O - 1.48 g Sodium Sulfate, 1.65 g Sodium Chloride to 1 liter of Distilled H_2O

4. Standards

a. Working Standards:

1. RDX Analysis:

93.44 mg RDX to 100 mL in Acetonitrile =
934.4 mg/L RDX Stock

Dilutions for Working Standards:

2.5 mL of stock to 100 mL	=	23.36 mg/L (I)
1.0 mL of (I) to 10 mL	=	2.336 mg/L (II)
5.0 mL of (I) to 100 mL	=	1.168 mg/L (III)
2.5 mL of (I) to 100 mL	=	584.0 µg/L (IV)
1.0 mL of (II) to 10 mL	=	233.6 µg/L (V)
1.0 mL of (III) to 10 mL	=	116.8 µg/L (VI)
1.0 mL of (IV) to 10 mL	=	58.4 µg/L (VII)
5.0 mL of (VII) to 10 mL	=	29.2 µg/L (VIII)

All dilutions of stock were made using methylene chloride as working solvent.

2. TNT, 2,4-DNT, 2,6-DNT Analyses:

TNT - 0.01423 g weighed into 100 mL volumetric = 142.3 mg/L (I)
2,4-DNT - 0.01416 g weighed into 100 mL volumetric = 141.6.mg/L (II)
2,6-DNT - 0.1849 g weighed into 100 ml volumetric = 184.9 mg/L (III)

All standards made up with benzene.

2.5 mL of (I), (II), (III) to 100 mL (A) =

TNT	3.56 mg/L
2,4-DNT	3.54 mg/L
2,6-DNT	4.62 mg/L

2.0 mL of (A) to 10 mL (B) = TNT 712 µg/L
2,4-DNT 706 µg/L
2,6-DNT 924 µg/L

5.0 mL of (A) to 10 mL (B) = TNT 356 µg/L
2,4-DNT 354 µg/L
2,6-DNT 462 µg/L

6.7 mL of (C) to 10 mL (D) = TNT 239 µg/L
2,4-DNT 237 µg/L
2,6-DNT 310 µg/L

5.0 mL of (C) to 10 mL (E) = TNT 178 µg/L
2,4-DNT 177 µg/L
2,6-DNT 231 µg/L

1.0 mL of (E) to 10 mL (F) = TNT 17.8 µg/L
2,4-DNT 17.7 µg/L
2,6-DNT 23.1 µg/L

1.0 mL of (B) to 10 mL (G) = TNT 71 µg/L
2,4-DNT 71 µg/L
2,6-DNT 92.4 µg/L

1.0 mL of (G) to 10 mL (H) = TNT 7.1 µg/L
2,4-DNT 7.1 µg/L
2,6-DNT 9.2 µg/L

b. Control Spikes:

Preparation of Spike Solutions:

TNT - 0.01287 g weighed into 100 mL volumetric = 128.7 mg/L (I)
2,4-DNT - 0.01431 g weighed into 100 mL volumetric = 143.1 mg/L (II)
2,6-DNT - 0.01902 g weighed into 100 mL volumetric = 190.2 mg/L (III)

All above solutions made up with benzene.

RDX - 0.08040 g weighed into 100 mL volumetric with methanol = 804.0 mg/L (IV)

Using TNT (I), 2,4-DNT (II), 2,6-DNT (III) and RDX (IV):
7.0 mL of (I) to 100 mL with methanol = TNT 9.01 mg/L (A)
7.0 mL of (II) to 100 mL with methanol = 2,4-DNT 10.02 mg/L (B)
5.0 mL of (III) to 100 mL with methanol = 2,6-DNT 9.5 mg/L (C)
1.0 mL of (IV) to 100 mL with 15% methanol in standard H_2O = RDX 8.04 mg/L (D)

10.0 mL of (A), (B), (C) and (D) to 100 mL of 60% methanol and 31% standard H_2O (E) =
0.901 mg/L TNT
1.002 mg/L 2,4-DNT
0.951 mg/L 2,6-DNT
0.804 mg/L RDX

69% methanol and 31% standard H_2O were the volumes necessary to keep the benzene of the concentrated SARM standards in solution.

10 DL:		10 mL of (E) to 1 L =
	TNT	9.01 µg/L
	2,4-DNT	10.02 µg/L
	2,6-DNT	9.51 µg/L
	RDX	8.04 µg/L
5 DL:		5 mL of (E) to 1 L =
	TNT	4.51 µg/L
	2,4-DNT	5.01 µg/L
	2,6-DNT	4.76 µg/L
	RDX	4.02 µg/L
2 DL:		2 mL of (E) to 1 L =
	TNT	1.80 µg/L
	2,4-DNT	2.00 µg/L
	2,6-DNT	1.90 µg/L
	RDX	1.61 µg/L
1 DL:		1 mL of (E) to 1 L =
	TNT	0.90 µg/L
	2,4-DNT	1.00 µg/L
	2,6-DNT	0.95 µg/L
	RDX	0.80 µg/L
0.5 DL:		1 mL of (E) to 1 L =
	TNT	0.45 µg/L
	2,4-DNT	0.50 µg/L
	2,6-DNT	0.48 µg/L
	RDX	0.40 µg/L

Blank

5. Procedure

a. Preparation of the Sorbent Tubes: The sorbent used for removal of RDX, TNT, 2,4-DNT and 2,6-DNT from water is Porapak S. The Porapak S is pretreated by soxhlet extraction with acetone for at least 2 hours to remove contaminants. The wet sorbent is dried (either air dried or in a vacuum oven at 30°C) before loading into the tube. The tubes used to contain the sorbent are 5 mL disposable pipets (pyrex). Clean glass wool is placed in the bottom of the pipet by means of a glass rod. Approximately 1.1 grams (3 mL by volume) of Porapak S is added to the pipet via a funnel with a teflon connection. The pipet is tapped to settle the sorbent and a piece of glass wool is placed on top of the sorbent. The sorbent tube is clamped in the vertical position to a ring stand and the teflon tubing from the pump is attached to the top of the column via a swagelok fitting. The packed sorbent tube is then pretreated by pumping 50 mL of acetone and then 50 mL of distilled H_2O through the column. The pretreated columns are capped to prevent moisture loss and stored at room temperature until needed.

b. Sampling with Sorbent Tubes: The sorbent tube is clamped in the vertical position to a ring stand. The end caps removed and a piece of aluminum foil wrapped around the tube. The delivery end of the pump is connected to the sorbent tube by means of teflon tubing and a swagelok fitting. The teflon tubing from the suction end of the pump is placed in the water to be sampled. For QC, 1 liter of spiked standard water is pumped through the sorbent tube. This solution is covered with aluminum foil to prevent photodegradation of the explosives. Although the pumps are calibrated for constant delivery, it is best to accurately measure the water flowing through the sorbent tube by either pumping a measured volume through the tube or by measuring the volume from the tube. After the sorbent tube is loaded it is capped, wrapped tightly with aluminum foil, and stored at 4°C (for up to 4 weeks) to await analysis. The pump and tubing are rinsed by pumping 50 mL of acetone and then 50 mL of distilled H_2O through them.

c. Desorption of Sorbent Tubes:

The previously loaded sorbent tubes are removed from the refrigerator and allowed to equilibrate to room temperature. Nitrogen is then blown through the tubes for 10 minutes to remove excess water. The outside tip of the pipet is then cleaned by wiping with cotton soaked in acetone. This cleaning removes the paint from the pipet and any residual contamination acquired through handling the tubes. The tube is then clamped to a ring stand in the inverted position. A second pipet is attached to the sorbent tube via a 5/16 in. I.D. teflon sleeve. Ten mL of acetone are added to the upper pipet and allowed to gravity flow through the inverted sorbent tube (slight pressure from a pipet bulb may be required to initiate flow). A 7.5 mL volume of the eluate from the column is collected in a graduated centrifuge tube.

d. HPLC Analysis of RDX: Two mL of the 7.5 eluate are placed in a test tube and blown dry with nitrogen. The sample is reconstituted with 2 mL of methylene chloride. The solutions are loaded into LC autosampler vials. Inject 200 µL of solution onto the HPLC column in duplicate. Inject standards singly before and after samples.

e. GC-EC Analysis of TNT, 2,4-DNT and 2,6-DNT: One mL of the 7.5 mL eluate is diluted to 5 mL with benzene. Sodium sulfate is added to the solution to remove any residual water. The dry benzene solutions are loaded into GC autosampler vials. Inject 2 µL in duplicate. Run standards singly before and after samples.

f. Chromatograms for the RDX and TNT, 2,4-DNT and 2,6-DNT are presented in Figures C-1 and C-2.

6. Calculations

For RDX, a line is constructed via least squares computation from the six standards used for each day of the four days' runs. Peak height is used for computations. Two runs of each sample are averaged to produce the found concentration. The concentration of RDX from the sorbent is multiplied by (7.5 mL extract/1000 mL water) to give the found concentration in water.

For TNT, 2,4-DNT and 2,6-DNT on GC analysis, a standard curve is plotted for each chemical with peak area versus picograms injected. The found chemical concentration from the sorbent is multiplied by:

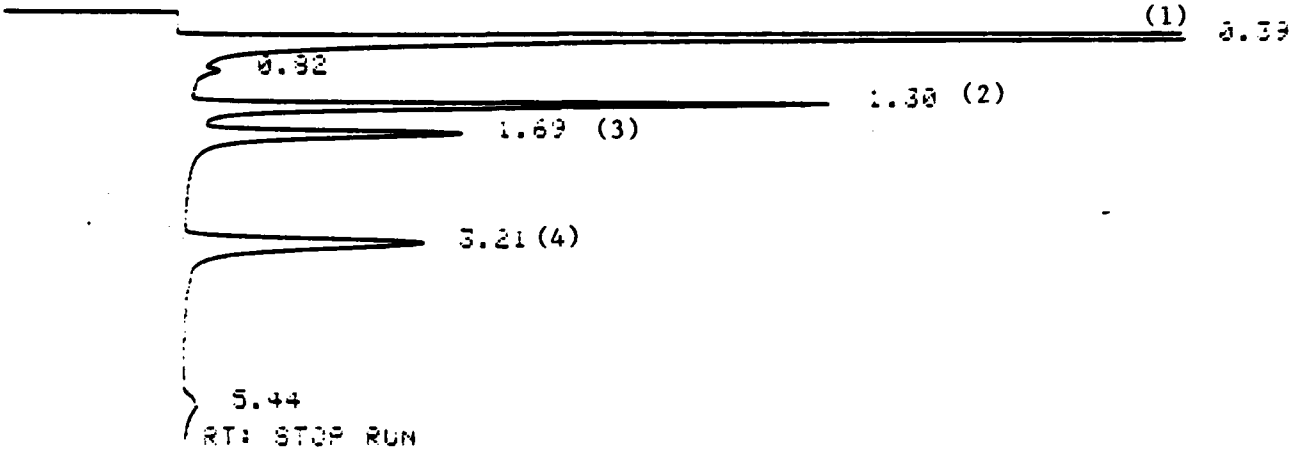
$$\frac{\text{(7.5 mL extract) (5 mL dilution)}}{\text{(1000 mL water)}},$$

to give the found concentration of TNT, 2,4-DNT and 2,6-DNT in water. The raw data and calculated values are presented in Tables C-1 to C-20 . The found versus target concentrations for the four days were evaluated for the RDX, TNT, 2,4-DNT and 2,6-DNT detection limits by the Hubaux and Vos (1975) formulae. In addition, the data were analyzed for standard deviation (Equation 1), percent imprecision (Equation 2), and percent inaccuracy (Equation 3). The detection limits for RDX, TNT, 2,4-DNT and 2,6-DNT, were 0.65, 1.50, 1.69 and 0.97 µg/L, respectively.

$$\text{standard deviation} = s = \left[\frac{n\Sigma x^2 - (\Sigma x)^2}{n(n-1)}\right]^{1/2} \qquad \text{Equation 1}$$

$$\text{percent imprecision} = s/\bar{x} \times 100 \qquad \text{Equation 2}$$

$$\text{percent inaccuracy} = \frac{\bar{x} - \text{ppb added}}{\text{ppb added}} \times 100 \qquad \text{Equation 3}$$



PEAKS

1 - Solvent
2 - 2,4-DNT - 1.3 min. 10 DL level
3 - 2,6-DNT - 1.7 min. 10 DL level
4 - TNT - 3.2 min. 10 DL level

Instrumentation - Gas Chromatograph - Hewlett-Packard 5880A with Computer Controller and Integrator
Auto Injector
Electron Capture Detector

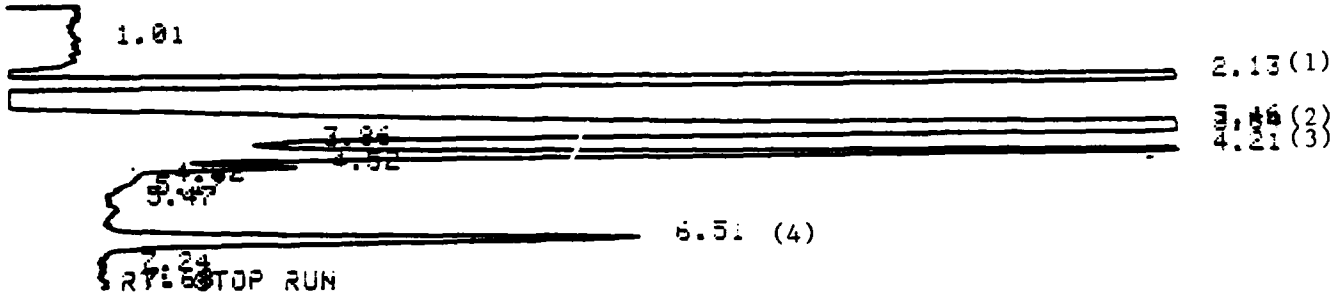
Column - 1.5% SP-2250/1.95% SP-2401 on 100/120 supelcoport packed in a 2 mm I.D., 0.25 in O.D. by 6 ft. column

Temperature - Injection Port - 210°C
Oven - 185°C
Detector - 300°C

Carrier Gas - N_2 at 28 cc/min

Injection Volume - 2 µL

Figure C-1. Sample Chromatogram of TNT, 2,4-DNT and 2,6-DNT from Sorbent Tube Eluate



PEAKS

1 - Solvent
2 - Impurity
3 - Impurity
4 - RDX - 6.5 min. - 10 DL level

Instrumentation - Perkin-Elmer LC601 with Perkin Elmer #LC-55 variable UV visible spectrometer
Hewlett-Packard 5880A GC integrator/recorder
Perkin-Elmer #LC-420 autosampler with rheodyne #7010 automated sampling valve with 200 µL sample loop

Column - Waters 10 micron silica column 10 cm x 7 mm radial compression cartridge

Mobile Phase - 61% hexane, 26% methylene chloride, 13% acetonitrile

Carrier Flow Rate - 1.5 mL/min.

UV Detector @ 232 nm

Figure C-2. Sample Chromatograph of RDX from Sorbent Tube Eluate

Table C-1. 2,4-DNT - Day 1

Concentration (µg/L)	Peak Area	Peak Areas of Spiked Samples		Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
		Injection 1	Injection 2			
7.1	770	594	500	25	.26	0
12.7	1495	1772	1831	25	.85	0.5
71	6203	2787	2722	25	1.28	1.0
177	11570	4406	4143	25	1.96	2.0
237	19143	9014	9093	25	5.11	5.01
355	27134	15995	16232	25	8.54	10.02

Table C-2. 2,4-DNT - Day 2

Concentration (µg/L)	Peak Area	Peak Areas of Spiked Samples Injection 1	Injection 1	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
17.7	1400	349	371	25	.17	0
71	6188	1593	1103	25	.60	0.5
177	11857	2771	2765	25	1.29	1.0
71	10662*	14726	14522	25	4.38	5.01
177	20077*	35489	30291	25	8.65	10.02
237	34846*					

*Run with 5 and 10 DL

Table C-3. 2,4-DNT - Day 3

Concentration (µg/L)	Peak Area	Peak Areas of Spiked Samples Injection 1	Peak Areas of Spiked Samples Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
0	0	597	640	25	.32	0
17.7	1355	1035	1767	25	.82	0.5
71	6662	2572	2780	25	1.20	1.0
177	13373	4610	5158	25	2.04	2.0
237	24489	10764	12183	25	5.57	5.01
		21128	24209	25	8.54	10.02

Table C-4. 2,4-DNT - Day 4

Concentration (µg/L)	Peak Area	Peak Areas of Spiked Samples Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
0	0	633	825	25	.40	0
17.7	1246	1028	2030	25	.93	0.5
71	5772	2778	3326	25	1.47	1.0
177	11464	4463	5510	25	2.37	2.0
237	20419	9613	11496	25	6.03	5.01
		18706	21675	25	8.95	10.02

Table C-5. 2,4-DNT

Data Summary

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	.26	.17	..32	.40	.29	.097	33.8	
0.5	.85	.60	.82	.93	.80	.14	17.6	60.0
1.0	1.28	1.29	1.20	1.47	1.31	.11	8.7	31.0
2.0	1.96	1.96	2.04	2.37	2.08	.20	9.4	4.1
5.01	5.11	4.38	5.57	6.03	5.27	.70	13.3	5.2
10.02	8.54	8.65	8.54	8.95	8.67	.19	2.2	-13.5

$Y = 0.8469X + 0.4552$

Y = 2,4-DNT concentration µg/L

X = peak area

Correlation coefficient = .9916

Detection limit = 1.69 µg/L

Table C-6. 2,6-DNT - Day 1

Concentration (µg/L)	Peak Area	Feak Areas of Spiked Samples Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
9.25	2323	1043	921	25	.21	0
23.1	4355	3766	3864	25	.81	.48
92.5	18189	5942	5887	25	1.23	.95
231	34741	9831	9501	25	1.99	1.90
308	59890	21441	21561	25	4.83	4.76
462.5	88502	38905	38895	25	9.76	9.51

Table C-7. 2,6-DNT - Day 2

Concentration (µg/L)	Peak Area	Peak Areas of Spiked Samples Injection 1	Injection 1	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/1)
9.25	2115	709	743	25	.16	0
23.1	4039	3414	2424	25	.59	.48
92.5	17790	5997	6097	25	1.28	.95
231	34772	9377	9585	25	1.97	1.90
92.5	30942*	34954	34509	25	4.14	4.76
231	62570*	76481	75940	25	9.59	9.51
308	121310*					

*Run with 5 and 10 DL

Table C-8. 2,6-DNT - Day 3

Concentration (µg/L)	Peak Area	Peak Areas of Spiked Samples Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/1)	Target Concentration (µg/L)
9.25	2440	0	0	25	0	0
23.1	4460	3504	3736	25	.74	.48
92.5	20668	5864	6341	25	1.16	.95
231	42754	11571	12695	25	2.14	1.90
308	83883	26977	30050	25	5.38	4.76
		54045	62781	25	9.79	9.51

Table C-9. 2,6-DNT - Day 4

Concentration (µg/L)	Peak Areas	Peak Areas of Spiked Samples Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
9.25	2002	0	0	25	0	0
23.1	4091	3336	4043	25	.79	.48
92.5	18858	5959	7014	25	1.30	.95
231	38241	11510	13251	25	2.35	1.90
308	71531	25039	28892	25	5.68	4.76
		49958	56497	25	9.99	9.51

Table C-10. 2,6-DNT

Data Summary

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	.21	.16	0	0	.09	.11	117.6	
.48	.81	.59	.74	.79	.73	.10	13.6	52.6
.95	1.23	1.28	1.16	1.30	1.24	.06	5.0	30.8
1.90	1.99	1.97	2.18	2.35	2.11	.18	8.3	11.2
4.76	4.83	4.14	5.38	5.68	5.01	.68	13.5	5.2
9.51	9.76	9.59	9.79	9.97	9.78	.16	1.6	2.9

Y = 1.0088 + 0.1988

Y = 2,6-DNT concentration µg/L

X = peak area

Correlation coefficient = .9969

Detection limit = 0.97 µg/L

Table C-11. TNT - Day 1

Concentration (µg/L)	Peak Area	Peak Areas of Spiked Samples Injection 1	Peak Areas of Spiked Samples Injection 1	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
7.1	759	206	115	25	.08	0
17.8	1404	1121	1215	25	.59	.45
71	6885	2048	1952	25	.94	.90
178	13877	3205	3023	25	1.38	1.80
239	23743	9258	9310	25	4.33	4.51
356	34496	17529	17775	25	8.05	9.01

Table C-12. TNT - Day 2

Concentration (µg/L)	Peak Area	Peak Areas of Spiked Samples Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
17.8	1226	1258	1337	25	.68	0
71	6528	719	695	25	.41	.45
71	11735*	2119	1985	25	.99	.90
178	23363*	3609	3501	25	1.57	1.80
239	42195*	15890	15966	25	4.13	4.51
		35489	35283	25	8.48	9.01

*Run with 5 and 10 DL

Table C-13. TNT - Day 3

Concentration (µg/L)	Peak Area	Peak Areas of Spiked Samples Injection 1	Injection 1	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
0	0	5	44	25	.01	0
17.8	1111	882	1031	25	.60	.45
71	6732	1840	1974	25	1.02	.90
178	14640	3874	4546	25	1.81	1.80
239	28219	10821	12556	25	5.21	4.51
		22792	26844	25	8.33	9.01

Table C-14. TNT - Day 4

Concentration (µg/L)	Peak Area	Peak Areas of Spiked Samples Injection 1	Injection 1	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
0	0	68	224	25	.10	0
17.8	947	721	1149	25	.66	.45
71	5786	1706	2298	25	1.11	.90
178	12468	3844	4876	25	2.10	1.80
239	23824	9501	12012	25	5.64	4.51
		20214	24668	25	8.63	9.01

Table C-15. TNT

Data Summary

Target Concentration (µg/L)	Found Concentration, µg/L Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	.08	.68	.01	.10	.22	.31	140.7	
.45	.59	.41	.60	.66	.57	.11	19.1	25.6
.90	.95	.99	1.02	1.11	1.02	.07	7.0	12.8
1.80	1.38	1.57	1.81	2.10	1.72	.31	18.1	-4.7
4.51	4.33	4.13	5.21	5.64	4.83	.72	14.8	7.0
9.01	8.05	8.48	8.33	8.63	8.37	.25	3.0	-7.1

$Y = 0.9255X + 0.2140$

Y = TNT concentration in µg/L

X = peak area

Correlation Coefficient = 0.9918

Detection Limit = 1.50 µg/L

Table C-16. RDX - Day 1

Concentration (µg/L)	Peak Height	Peak Areas of Spiked Samples Injection 1	Injection 1	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
0	0	0	0	133.3	0	0
29.2	7.8	11.6	9.4	133.3	.42	.402
58.4	11.4	19.8	18.7	133.3	.83	.804
116.8	20.7	33.1	34.1	133.3	1.51	1.608
233.6	39.3	79.8	76.4	133.3	3.61	4.02
584	93.1	134.7	137.9	133.3	6.35	8.04
1168	187.2					
2336	373.2					

Table C-17. RDX - Day 2

Concentration (µg/L)	Peak Areas	Peak Areas of Spiked Samples Injection 1	Peak Areas of Spiked Samples Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
29.2	5.4	0	0	133.3	0	0
58.4	10.1	9.2	7.7	133.3	.31	.402
116.8	20.1	17.8	17.8	133.3	.79	.804
233.6	37.3	40.2	37.5	133.3	1.86	1.608
584	89	77.5	75.6	133.3	3.79	4.02
1168	175	135.0	126.1	133.3	6.54	8.04
2336	345					

Table C-18. RDX - Day 3

Concentration (µg/L)	Peak Areas	Peak Areas of Spiked Samples Injection 1	Peak Areas of Spiked Samples Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
29.2	6.8	0	0	133.3	0	0
58.4	11	7.2	7.2	133.3	.25	.402
116.8	19.8	15.3	13.2	133.3	.60	.804
233.6	37.5	33.3	30.9	133.3	1.49	1.608
584	89.6	83.2	81.5	133.3	3.97	4.02
1168	181.1	118.1	129.4	133.3	6.02	8.04
2336	356.1					

Table C-19. RDX - Day 4

Concentration (µg/L)	Peak Height	Peak Height of Spiked Samples Injection 1	Peak Height of Spiked Samples Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
29.2	6.0	0.	0.	133.3	0	0
58.4	14.7	12.7	12.7	133.3	.34	.402
116.8	23.5	20.6	19.0	133.3	.70	.804
233.6	41.0	43.2	41.8	133.3	1.84	1.608
584	95.8	94.4	93.4	133.3	4.41	4.02
1168	187	143.5	143.8	133.3	6.90	8.04
2336	353					

Table C-20. RDX

Data Summary

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	0	0	0	0	0	0		
.402	.42	.31	.25	.34	.33	.07	21.4	-17.9
.804	.83	.79	.60	.70	.73	.10	14.0	- 9.2
1.608	1.51	1.86	1.49	1.84	1.68	.20	12.1	4.2
4.02	3.61	3.79	3.97	4.41	3.95	.34	8.7	- 1.9
8.04	6.35	6.54	6.02	6.90	6.45	.37	5.7	-19.7

Y = 0.816X + 0.107; Detection Limit = 1.53 µg/L; Correlation Coefficient = 0.9897 (all data 0 - 10 DL)

Y = 0.992X + 0.0169; Detection Limit = 0.64 µg/L; Correlation Coefficient = 0.9930 (0 - 5 DL data only)

B. Analysis of Low Levels of Tetryl in Water with the Use of Solid Sorbent Tubes - Quantitative

1. Application

Method used to determine the concentration of tetryl in water using solid sorbent tubes.

a. Tested Concentration Range: (µg/L)

Tetryl - 0.74 to 14.78 µg/L

b. Sensitivity:

Tetryl - 56.7 area units/pg based on a 132.5 pg injection

c. Detection Limit: (µg/L)

Tetryl - 1.42 µg/L

d. Interferences: Contaminants in sorbents must be removed by soxhlet extraction with acetone before use.

e. Analysis Rate: With two pumps, 8 samples can be collected, run, and analyzed per day.

2. Chemistry

$C_7H_5N_5O_3$	Tetryl, Aniline, N-methyl-2,4,6-tetra-nitro
CAS RN	479-45-8
Melting Point:	131°C
Boiling Point:	187°C (Explodes)

Hazards: Use caution in handling tetryl, explosive and toxic hazards exists.

3. Apparatus

a. Instrumentation:

Gas Chromagotraph - Varian 3700 with an electron capture detector and a Varian 8000 autosampler
Hewlett-Packard 5880A GC Integrator/Recorder

b. Parameters

Column - 1.5% SP-2250/1.95% SP-2401 on 100/120 supelcoport packed in a 2 mm I.D., 0.25 in O.D. by 6 ft. column
Temperature - Injection Port - 210°C
Oven - 200°C
Detector - 300°C
Carrier Gas - Nitrogen at 28 cc/minute
Detector - Electron Capture
Injection Volume - 2 µL
Retention Time - 4.5 minute

c. Glassware/Hardware

Volumetric Flask - 1000 mL (8)
Volumetric Flask - 100 mL (3)
Volumetric Flask - 10 mL (5)
Beaker - 1000 mL (1)
Pipet, Disposable - 10 mL (4)
Pipet, Disposable - 5 mL (64)
Pipet, Disposable - 1 mL (16)
Graduated Centrifuge Tubes (24)
GC Autosampler vials with teflon lined screw caps
Teflon Tubing for PUmp
Teflon Sleeve - 5/16 in I.D. (6)
Applied Science - Purified Amberlite XAD-4 polystylene resin, mesh 20/60, #17314
Aluminum Foil
Ring Stands (6)
Clamps (6)
Funnel, Glass (1)
Refrigerator
10 µL Hamilton Syringe (1)
Analytical Balance

d. Chemicals

Tetryl "SARM", PA 588, Lot #2714
Methanol - HPLC Certified Grade
Acetone - Fisher Scientific certified
Benzene - Fisher Scientific certified
Standard H_2O - 1.48 g sodium sulfate, 1.6 g sodium chloride to 1 liter of distilled H_2O

4. Standards

a. Calibration Standards:

26.54 mg tetryl weighed into 100 mL volumetric and brought to volume with benzene = 265.4 mg/L stock

1.0 mL stock to 100 mL	=	2.65 mg/L (I)
5.0 mL (I) to 10 mL	=	1.325 mg/L (II)
2.5 mL (I) to 10 mL	=	662.5 µg/L (III)
1.0 mL (II) to 10 mL	=	132.5 µg/L (IV)
1.0 mL (II) to 20 mL	=	66.3 µg/L (V)
1.0 mL (IV) to 10 mL	=	13.3 µg/L VI)

All dilutions of stock were made using benzene the working solvent.

b. Control Spikes:

29.56 mg tetryl weighed into 100 mL volumetric and brought to volume with benzene = 295.6 mg/L stock

5 mL of 295.6 mg/L stock to 1000 mL with 55:45 methanol/water = 1.478 mg/L (A)

10 DL:	10 mL (A) to 1 L	=	14.78 µg/L
5 DL:	5 mL of (A) to 1 L	=	7.39 µg/L
2 DL:	2 mL (A) to 1 L	=	2.96 µg/L
1 DL:	1 mL (A) to 1 L	=	1.48 µg/L
0.5 DL:	0.5 mL (A) to 1 L	=	0.74 µg/L
Blank			

All dilutions are made with standard water.

5. Procedure

a. Preparation of the Sorbent Tubes: The sorbent used for removal of tetryl from water is XAD-4. The XAD-4 is pretreated by soxhlet extraction with acetone for at least 2 hours to remove contaminants. The wet sorbent is dried (either air dried on in a vacuum oven at 30°C) before loading into the tube. The tubes used to contain the sorbent are 5 mL disposable pipets (pyrex). Clean glass wool is placed in the pipet by means of a glass rod. Approximately 1.2 grams (3 mL by volume) of XAD-4 is added to the pipet via a funnel with a teflon connection. The pipet is tapped to settle the sorbent and a piece of glass wool is placed on top of the sorbent. The sorbent tube is clamped in the vertical position to a ring stand and the teflon tubing from the pump is attached to the top of the column via a swagelog fitting. The packed sorbent tube is then pretreated by pumping 50 mL of acetone and then 50 mL of distilled H_2O through the column. The pretreated columns are then capped to prevent moisture loss and stored at room temperature until needed.

b. Sampling with Sorbent Tubes: The sorbent tube is clamped in the vertical position, the end cap removed, and a piece of aluminum foil is wrapped around the tube. The delivery end of the pump is connected to the sorbent tube by means of teflon tubing and a swagelok fitting. The teflon tubing from the suction end of the pump is placed in the water to be sampled. For QC, 1 liter of spiked standard water is pumped through the sorbent tube. This solution is covered with aluminum foil to prevent photodegradation of the explosive. Although the pumps are calibrated for constant delivery, it is best to accurately measure the water flowing through the sorbent tube by either pumping a measured volume through the tube or measuring the volume from the tube. After the sorbent tube is loaded, it is capped, wrapped tightly with aluminum foil, and stored at 4°C (for up to 4 weeks) to await analysis. The pump and tubing are rinsed by pumping 50 mL of acetone and then 50 mL of distilled water through them.

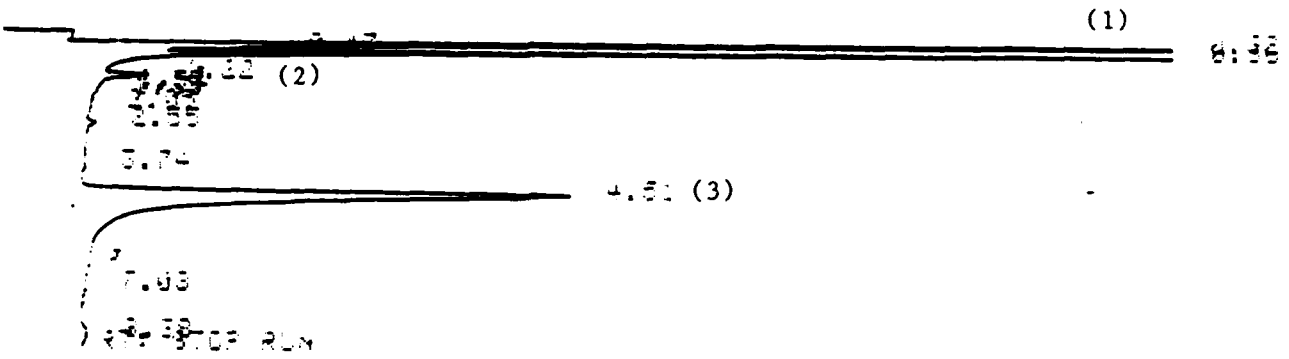
c. Desorption of Sorbent Tubes and Analysis: The previously loaded sorbent tubes are removed from the refrigerator and allowed to equilibrate to room temperature. Nitrogen is then blown through the tubes for 10 minutes to remove excess water. The outside tip of the sorbent is then cleaned by wiping with cotton soaked in acetone. This cleaning removes the paint from the pipet and any residual contamination acquired through handling the tubes. The tube is then clamped to a ring stand in the inverted position. A second pipet is attached to the sorbent tube via a 5/16 in. I.D. teflon sleeve. One mL of methanol is added to the upper pipet and forced into the sorbent tube with pressure from a pipet bulb. Ten mL of benzene are then added to the upper pipet and allowed to gravity drain through the sorbent tube. The initial 7.5 mL of eluate are collected in a graduated centrifuge tube. The collected liquid is mixed well, centrifuged. The upper benzene layer is measured and the volume recorded. The benzene layer is carefully removed with a 5 mL pipet and 2 mL are placed in a GC autosampler vial.

Inject 2 µL of the sample onto the GC column in duplicate. Inject standards singly before and after each run.

d. A sample chromatogram is presented in Figure C-3.

6. Calculations

Concentrations of each sample are obtained by point to point interpolation from a standard curve plotted with area versus µg/L injected. Found concentrations are calculated as follows:



PEAKS

1 - Solvent
2 - Impurity
3 - Tetryl - 4.5 min. 2 DL level

Instrumentation - Gas Chromatograph - Varian 3700 with Hewlett-Packard 5880A
Computer Controller and Integrator
Auto Injector
Electron Capture Detector

Column - 1.5% SP-2250/1.95% SP-2401 on 100/120 supelcoport packed in a 2 mm I.D., 0.25 in. O.D. by 6 ft. column

Temperature - Injection Port - 210°C
Oven - 200°C
Detector - 300°C

Carrier Gas - N_2 @ 28 cc/min.

Injection Volume - 2 µL

Figure C-3. Sample Chromatogram of Tetryl from Sorbent Tube Eluate

Found Concentration =

$$\mu g/L \text{ (extract)} \times \frac{\text{Volume (benzene)}}{1000 \text{ mL}}$$

The raw data and calculated values are presented in Tables C-21 to C-25. The found versus target concentrations for the four days were evaluated for tetryl detection limit by the Hubaux and Vos (1975) formulae. In addition, the data were analyzed for standard deviation (Equation 1), percent imprecission (Equation 2), and percent inaccuracy (Equation 3). The detection limits for tetryl was 1.42 µg/L.

$$\text{standard deviation} = s = \left[\frac{n\Sigma x^2 - (\Sigma x)^2}{n(n-1)}\right]^{1/2} \qquad \text{Equation 1}$$

$$\text{percent imprecision} = s/\bar{x} \times 100 \qquad \text{Equation 2}$$

$$\text{percent inaccuracy} = \frac{\bar{x} - \text{ppb added}}{\text{ppb added}} \times 100 \qquad \text{Equation 3}$$

Table C-21. Tetryl - Day 1

Concentration (µg/L)	Peak Areas 1	Peak Areas 2	Peak Areas of Spiked Samples Injection 1	Peak Areas of Spiked Samples Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
13.25	657	680	107	587	172.4	0.02	0
66.25	6,627	8,401	9,088	8,828	161.3	0.49	0.74
132.5	14,163	16,840	23,703	22,094	188.7	0.97	1.48
662.5	102,269	87,233	55,885	54,382	166.7	2.37	2.96
1,325	301,271	300,098	330,667	331,578	194.2	7.40	7.39
2,650	709,235	666,540	427,660	408,776	163.9	10.52	14.78

Table C-22. Tetryl - Day 2

Concentration (µg/L)	Peak Areas 1	Peak Areas 2	Peak Areas of Spiked Samples Injection 1	Peak Areas of Spiked Samples Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
13.25	598	780	225	185	151.5	0.01	0
66.25	7,514	7,480	7,398	7,801	152.7	0.44	0.74
132.5	15,283	15,612	21,994	21,600	156.3	1.12	1.48
662.5	94,380	97,996	69,131	68,708	165.3	2.94	2.96
1,325	298,002	308,512	315,490	309,218	151.5	9.00	7.39
2,650	689,235	690,200	657,342	674,452	183.5	14.01	14.78

Table C-23. Tetryl - Day 3

Concentration (µg/L)	Peak Areas 1	Peak Areas 2	Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
13.25	1,695	1,582	0	76	169.5	0	0
66.25	8,850	9,357	14,340	13,492	172.4	0.59	0.74
132.5	17,888	18,401	28,561	28,770	172.4	1.15	1.48
331.25	49,978	50,159	74,452	72,096	169.5	2.61	2.96
662.5	118,470	120,737	300,365	300,891	161.3	7.62	7.39
1,325	327,282	335,232	569,718	558,160	149.3	16.04	14.78
2,650	614,917	624,570					

Table C-24. Tetryl - Day 4

Concentration (µg/L)	Peak Areas 1	Peak Areas 2	Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
13.25	1,610	1,648	119	245	163.9	0.01	0
66.25	8,751	9,382	14,148	14,487	169.5	0.61	0.74
132.5	18,003	18,288	28,853	28,114	161.3	1.22	1.48
331.25	51,028	49,411	100,691	103,873	158.7	3.65	2.96
662.5	118,507	120,638	336,950	337,659	181.8	7.44	7.39
1,325	330,292	313,768	668,390	658,329	178.6	15.9	14.78
2,650	623,584	612,453					

Table C-25. Detection Limit Data Summary for Tetryl

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	.02	.01	.00	.01	.01	.01	0	
.74	.49	.44	.59	.61	.53	.08	15.2	-28.0
1.48	.97	1.12	1.15	1.22	1.12	.11	9.4	-24.7
2.96	2.37	2.94	2.61	3.65	2.89	.56	19.2	- 2.3
7.39	7.40	9.00	7.62	7.44	7.86	.76	9.7	6.4
14.78	10.52	14.01	16.04	15.90	14.12	2.57	18.2	- 4.5

Y = 0.978X - 0.0378; Detection Limit = 3.86 µg/L; Correlation Coefficient = 0.9801 for all data (0-10 DL)

Y = 1.0867X - 0.2495; Detection Limit = 1.42 µg/L; Correlation Coefficient = 0.9901 for (0-5 DL)

C. Analysis of Low Levels of Nitroglycerine and PETN in Water With the Use of Solid Sorbent Tubes - Quantitative

1. Application

Method used to determine the concentration of nitroglycerine and PETN in water using solid sorbent tubes.

a. Tested Concentration Range: (µg/L)

Nitroglycerine - 2.54 to 50.7 µg/L
PETN - 2.57 to 51.4 µg/L

b. Sensitivity:

Nitroglycerine - .66 peak ht units/ng based on 52.8 ng injection
PETN - 1.08 peak ht units/ng based on 42.8 ng Injection

c. Detection Limits:

Nitroglycerine - 6.94 µg/L
PETN - 8.96 µg/L

d. Interferences: Significant interferences are observed if the Porapak R resin is not thoroughly cleaned before sampling. Soxhlet extract of the sorbent with acetone followed by pumping acetone through the packed tubes until the filtrate is clean is highly recommended. Cleaning of previously used resins is easier than cleaning new resin.

e. Analysis Rate: With two pumps, 8 samples can be collected, desorbed and analyzed each day.

2. Chemistry

$C_3H_5N_3O_9$	propanetrioltrinitrate, nitroglycerine
CAS RN	55-63-0
Melting Point	13.2°C
Boiling Point	180°C @ 50 mm Hg
	145°C decomposes @ 760 nm Hg
$C_5H_8N_4O_{12}$	2,2-bis(hydroxymethyl)-1,3-propane-dioltetranitrate, PETN
CAS RN	78-11-5
Melting Point	141.3°C
Boiling Point	180°C @ 50 mm Hg

Hazards. Use extreme caution in handling these compounds. Explosive and toxic hazards exist.

3. Apparatus

a. Instrumentation:

HPLC - Perkin Elmer #LC-601 with Perkin Elmer #LC55 variable UV-visible spectrometer
Hewlett-Packard 5880A GC integrator/recorder
Perkin Elmer #LC-420 autosampler with rheodyne #7010 automated sampling valve with 200 µL sample loop.

b. Parameters:

Column - Waters radial compression column (10 cm x 7 mm I.D.), 10 micron silica
Carrier Solvent - 2.5% isopropanol/ 97.5% hexane. Before use, solvent is filtered through a 0.45 micron non-aqueous membrane filter using a millipore filtration apparatus. Solvent is then degassed in the delivery cylinder using a helium sparger.
Flow Rate - 2 mL/min.
UV detector @ 204 nm
Retention Time - PETN 4.9 min.
NG 6.7 min.

c. Hardware/Glassware:

Volumetric Flasks - 1000 mL (7)
Volumetric Flasks - 100 mL (8)
Volumetric Flasks - 10 mL (3)
Pipet, disposable - 1 mL (32)
Pipet, disposable - 5 mL (44)
Pipet, disposable - 10 mL (16)
Flask, 4 liter (1) for mixing LC carrier solvent
GC autosampler vials with teflon lined caps
Slo-syn synchronous stepping motor FMI-LAB pump model #SS50-1296
Teflon tubing for pump
Graduated Cylinder - 25 mL (6)
Aluminum foil
Millipore filter apparatus (1)
0.45 micron non-aqueous millipore filters
Gas sparger (1)
10 µL Hamilton syringe (1)
Refrigerator
Analytical balance
Ring stands (6)
Clamps (6)
Funnel, glass (1)
Glass wool
Pasteur pipets (44)
Silli Evaporator
Waters Associates Porapak R - 100/120 mesh

d. Chemicals:

Nitroglycerine - SARM #PA 596, for both control spikes and working standards
PETN - SARM, #PA 604, for both control spikes and working standards
Acetonitrile HPLC Grade (Fisher)
Acetone, Fisher certified
Hexane, Fisher HPLC Grade
Isopropanol Fisher HPLC Grade
Helium (purified)
Nitrogen (regular grade)
Standard H_2O 1.48 g Na_2SO_4 to 1 liter of
1.65 g NaCl distilled H_2O

4. Standards

Primary Standard Stocks

85.60 mg PETN SARM to 100 mL in Acetonitrile = 855 mg/L
105.66 mg NG SARM to 100 mL in Acetonitrile = 105.6 mg/L

a. Working Standards:

(I) 5 mL of each stock to 100 mL = 42.8 mg/L PETN
52.8 mg/L NG

This dilution was in Isopropanol. All subsequent dilutions were in hexane.

12.5 mL (I) to 100 mL	=	5.35 mg/L PETN (II)
		6.60 mg/L NG
10.0 mL (I) to 100 mL	=	4.28 mg/L PETN (III)
		5.28 mg/L NG
5 mL (I) to 100 mL	=	2.14 mg/L PETN (IV)
		2.64 mg/L NG
2.5 mL (I) to 100 mL	=	1.07 mg/L PETN (V)
		1.32 mg/L NG
1 mL (III) to 10 mL	=	.428 mg/L PETN (VI)
		.528 mg/L NG
1 mL (IV) to 10 mL	=	.214 mg/L PETN (VII)
		.264 mg/L NG
1 mL (V) to 10 mL	=	.107 mg/L PETN (VIII)
		.132 mg/L NG

b. Control Spikes:

1.0 mL PETN stock
.8 mL NG stock were brought to 100 mL with standard H_2O
10 mL Acetonitrile

Acetonitrile was used to insure solution of PETN, NG. This yield a spiking stock = 8.56 mg/L PETN (I)
8.45 mg/L NG
This solution should be freshly prepared on a daily basis due to decomposition of PETN.

To obtain final concentration in H_2O, the volume of stock specified was added to 1 liter of standard H_2O.

10 DL = 6 mL of (I) to 1 L =
PETN 51.4 µg/L
NG 50.7 µg/L

5 DL = 3 mL of (I) to 1 L =
PETN 25.7 µg/L
NG 25.4 µg/L

2 DL = 1.2 mL of (I) to 1 L =
PETN 10.3 µg/L
NG 10.1 µg/L

1 DL = .6 mL of (I) to 1 L =
PETN 5.14 µg/L
NG 5.07 µg/L

.5 DL = .3 mL of (I) to 1 L =
PETN 2.57 µg/L
NG 2.54 µg/L

5. Procedure

a. *Preparation of Sorbent Tubes:* Porapak R is the sorbent used for removing PETN and NG from water. The Porapak R is pretreated by soxhlet extraction with acetone for 2 - 2 1/2 hours and then dryed at 30°C in vacuum oven. Glass wool is placed in the bottom of 5 mL disposable pipet (pyrex) and approximately 1.1 g of Porapak R (3 mL by volume) are added. The column is tapped to settle the sorbent and a glass wool plug is placed on top of the sorbent. The packed sorbent tube is pretreated by pumping several hundred mL of acetone (or until the filtrate is free of impurities) and then 50 mL of distilled H_2O through the tube. The pretreated columns are capped to prevent moisture loss and stored at room temperature until needed.

b. Sampling with Sorbent Tubes: The sorbent tube is clamped in a vertical position to a ring stand. The end caps removed and a piece of aluminum foil wrapped around the tube. The delivery end of the pump is connected to the sorbent tube using teflon tubing and Swagelok fittings. The teflon tubing on the suction side of the pump is placed in the water to be sampled. For QC, 1 liter of spiked standard water is pumped through the sorbent tube. This solution is covered in aluminum foil to prevent photodegradation of the explosives. Although the pumps are calibrated for constant delivery, it is best to accurately measure the water flowing through

the sorbent tube by either pumping a measured volume through the tube or by measuring the volume from the tube. A flow rate of 5 mL/min is recommended. After the sorbent tube is loaded, it is capped and tightly wrapped in aluminum foil and stored at 4°C (for up to 4 weeks) to await analysis. The pump and tubing are rinsed by pumping 50 mL acetone followed by 50 mL distilled water through them.

c. Desorption of Sorbent Tubes: The loaded sorbent tubes are removed from the refrigerator and allowed to come to room temperature. Nitrogen is blown through them to remove as much water as possible. The loaded tubes are then placed back on the pumps used for loading the tubes and acetone is pumped through them. The first 20 drops of liquid coming out of the tube are discarded since they are mostly water. The next 20 mL of acetone are collected in a graduated cylinder and transferred to a screw cap vial. Four mL of the acetone solution are blown to dryness with nitrogen.and reconstituted to 2 mL with hexane. The hexane solutions are loaded into LC autosampler vials. A 200 µL loop injection valve is used. Samples are injected in duplicate. Standards are injected singly before and after samples. A sample chromatograph is presented in Figure C-4.

6. Calculations

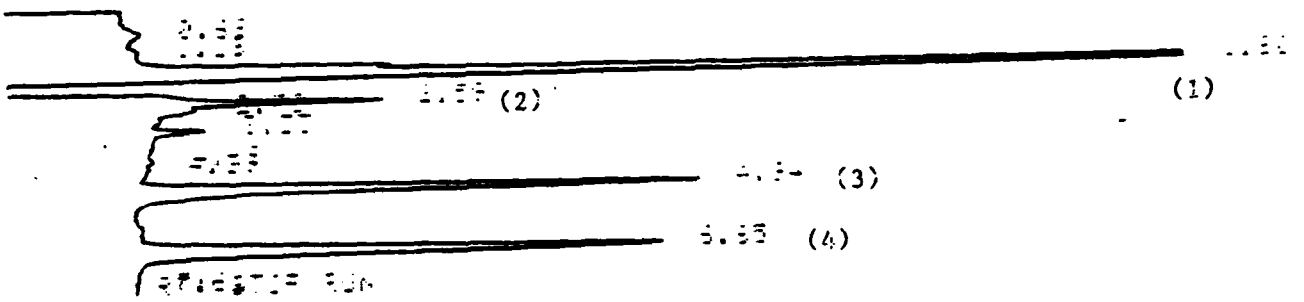
Lines were constructed via least squares computation from the seven standards for both PETN and NG for each of the four days runs. Peak height was used for the computations. Two runs of each sample were averaged to produce the found concentration. The concentration of PETN and NG were multiplied by (20 mL eluate x 2 concentration in solvent exchange/1000 mL H_2O).

The raw data and calculated values are presented in Tables C-26 to C-35. The found versus target concentrations for each chemical over the four days were evaluated for their detection limit by the Hubaux and Vos (1975) formulae. In addition, the data were analyzed for standard deviation (Equation 4), percent imprecision (Equation 5), and percent inaccuracy (Equation 6).

$$\text{standard deviation} = s = \left[\frac{n\Sigma x^2 - (\Sigma x)^2}{n(n-1)}\right]^{1/2} \qquad \text{Equation 1}$$

$$\text{percent imprecision} = s/\bar{x} \times 100 \qquad \text{Equation 2}$$

$$\text{percent inaccuracy} = \frac{\bar{x} - \text{ppb added}}{\text{ppb added}} \times 100 \qquad \text{Equation 3}$$



PEAKS

1 - Solvent
2 - Solvent
3 - PETN 5 DL level
4 - Nitroglycerine 5 DL level

Instrumentation - Perkin-Elmer LC601 with Perkin Elmer #LC-55 variable UV visible spectrometer
Hewlett-Packard 5880A GC integrator/recorder
Perkin-Elmer #LC-420 autosampler with rheodyne #7010 automated sampling valve with 200 µL sample loop

Column - Waters 10 micron silica column 10 cm x 7 mm radial compression cartridge

Mobile Phase - 2.5% isopropanol/97.5% hexane

Carrier Flow Rate - 2 mL/min.

UV Detector @ 204 nm

Figure C-4. Sample Chromatograph of PETN and Nitroglycerine from Sorbent Tube Eluate

Table C-26. PETN - Day 1

Concentration (mg/L)	Peak Height	Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
.107	23.6	0	0	100	0	0
.214	43.8	34.7	37.1	100	1.71	2.57
.428	89.7	74.02	79.3	100	3.68	5.14
1.07	225.4	144.8	140.5	100	6.86	10.3
2.14	441.5	347.6	348.0	100	16.74	25.7
4.28	884.9	633.6	615.2	100	30.08	51.4
5.35	1113.8					

Table C-27. PETN - Day 2

Concentration (mg/L)	Peak Height	Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
.107	23.6	0	0	100	0	0
.214	43.8	30.9	35.1	100	1.57	2.57
.428	89.7	38.9	38.6	100	1.85	5.14
1.07	225.4	106.9	101.5	100	5.0	10.3
2.14	441.5	274.3	272.0	100	13.5	25.7
4.28	884.9	567.6	544.8	100	26.79	51.4
5.35	1113.8					

Table C-28. PETN - Day 3

Concentration (mg/L)	Peak Height	Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
.107	23.6	0	0	100	0	0
.214	43.8	27.02	24.73	100	1.23	2.57
.428	89.7	54.3	51.8	100	2.54	5.14
1.07	225.4	102.9	107.8	100	5.06	10.3
2.14	441.5	292.3	282.5	100	13.83	25.7
4.28	884.9	517.8	503.4	100	24.59	51.4
5.35	1113.8					

Table C-29. PETN - Day 4

Concentration (mg/L)	Peak Height	Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
.107	24.9	0	0	100	0	0
.214	46.3	26.42	26.40	100	1.37	2.57
.428	91.8	56.41	54.05	100	2.73	5.14
1.07	224.0	106.7	97.33	100	4.93	10.3
2.14	438.7	260.5	244.7	100	12.03	25.7
4.28	880.0	536.7	503.4	100	24.64	51.4
5.35	1156.2					

Table C-30. PETN Data Summary

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	0	0	0	0	0	0		
2.57	1.71	1.57	1.23	1.37	1.47	0.21	14.4	-42.8
5.14	3.68	1.85	2.54	2.73	2.70	0.75	28.0	-47.5
10.30	6.86	5.00	5.06	4.93	5.46	0.93	17.1	-47.0
25.7	16.74	13.15	13.83	12.03	13.94	2.01	14.4	-45.8
51.4	30.08	26.79	24.59	24.64	26.53	2.58	9.7	-48.4

$Y = 0.5178X + 0.1409$

Correlation Coefficient = 0.9910

Detection Limit = 8.96 µg/L

Table C-31. Nitroglycerine - Day 1

Concentration (mg/L)	Peak Height	Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
.132	17.2	0	0	100	0	0
.264	34.2	30.4	30.1	100	3.07	2.54
.528	68.4	46.95	47.9	100	4.19	5.07
1.32	176.4	117.04	114.9	100	8.66	10.1
2.64	346.9	284.6	284.6	100	19.66	25.4
5.28	757.1	490.9	478.8	100	32.73	50.7
6.60	1035.2					

Table C-32 . Nitroglycerine - Day 2

Concentration (mg/L)	Peak Height	Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
.132	12.9	0	0	100	0	0
.264	33.7	21.1	24.3	100	2.81	2.54
.528	60.6	31.3	30.9	100	3.42	5.07
1.32	154.0	100.0	103.1	100	8.51	10.1
2.64	309.9	222.2	213.8	100	16.93	25.4
5.28	688.1	537.4	514.4	100	39.18	50.7
6.60	930.6					

Table C-33. Nitroglycerine - Day 3

Concentration (mg/L)	Peak Height	Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
.132	17.3	0	0	100	0	0
.264	34.5	22.2	18.2	100	2.41	2.54
.528	68.0	53.8	48.4	100	4.42	5.07
1.32	176.8	100.63	100.43	100	7.65	10.1
2.64	346.5	341.7	235.4	100	19.92	25.4
5.28	757.8	36.9	519.5	100	35.55	50.7
6.60	1035.3					

Table C-34. Nitroglycerine - Day 4

Concentration (mg/L)	Peak Height	Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
.132	17.6	0	0	100	0	0
.264	35.0	24.0	24.0	100	2.56	2.[illegible]
.528	68.1	46.64	43.93	100	4.03	5.[illegible]
1.32	168.1	108.9	103.9	100	8.25	10.1
2.64	337.4	241.1	227.6	100	17.09	25.4
5.28	717.8	483.6	453.1	100	33.25	50.7
6.60	978.8					

Table C-35. Nitroglycerine Data Summary

Target Concentration (µg/L)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	0	0	0	0	0	0	6.8	-10.7
2.54	3.07	2.81	2.41	2.56	2.71	0.29	10.7	-20.8
5.07	4.19	3.42	4.42	4.03	4.02	0.43	5.4	-18.1
10.10	8.66	8.51	7.65	8.25	8.27	0.45	8.7	-27.6
25.4	19.66	16.93	19.92	17.07	18.40	1.61	8.3	-30.62
50.7	32.73	39.18	35.55	32.55	35.18	2.94		

$Y = 0.684X + 0.7211$

Correlation Coefficient = 0.9944

Detection Limit = 6.94 µg/L

D. Analysis of Low Levels of Picric Acid in Water with the Use of Solid Sorbent Tubes- Quantitative

1. Application

Method used to determine the concentration of Picric Acid in water using solid sorbent tubes.

a. Tested Concentration (µg/L):

Picric Acid - 2.6 to 52.0 µg/L

b. Sensitivity:

Picric Acid - 3.6 peak height units/ng based on 26 ng injection

c. Detection Limit:

Picric Acid - 6.98 µg/L

d. Interferences: Contaminants from sorbents must be removed by soxhlet extraction with acetone before use. Also packed sorbent tubes should be pre-extracted with desorption solvent before loading.

e. Analysis Rate: With two pumps, eight samples can be collected, run and analyzed each day.

2. Chemistry

$C_6H_3N_3O_7$ Phenol, 2,4,6-trinitro
CAS RN 88-89-1
Melting Point: 122°C
Boilint Point: 300°C (explodes)

Hazards: Toxic and explosive hazards exist.

3. Apparatus

a. Instrumentation:

HPLC - Perkin-Elmer, #LC-601 with Perkin-Elmer, #LC-55 variable wavelength UV-visible spectrometer
Perkin-Elmer, #LC-420 Autosampler with Rheodyne #7010 loop injection valve and 200 µL sample loop.

b. Parameters:

Column - Waters 10 micron ODS Radial Compression Column (10 cm x 7 mm I.D.)
Mobile Phase 50% acetonitrile, 50% water, 0.005M tetrabutyl ammonium hydroxide buffered to pH 6.5 with phosphoric acid.
Flow Rate - 2.0 mL/min.
UV Detector at 205 nm
Retention Time - 4.6 min.
Before use, solvent is vacuum filtered through 0.45 micron non-aqueous membrane filter using millipore filtration apparatus. Solvent is then degassed in the delivery cylinder using a helium sparger.

c. Hardware/Glassware:

Volumetric Flasks - 1000 mL (7)
Volumetric Flasks - 100 mL (3)
Volumetric Flasks - 50 mL (1)
Volumetric Flasks - 10 mL (5)
Beaker - 1000 mL (2)
Pipet, disposable - 1 mL (20)
Pipet, disposable - 5 mL (44)
Pipet, disposable - 10 mL (21)
Pipet, disposable - 25 mL (4)
Pipet, disposable - 50 mL (4)
Erlnmeyer Flask - 4000 mL (1) (for LC solvents)
Graduated Centrifuge Tubes
GC Autosampler Vials with Teflon-lined seals
Slo-Syn Synchronous Tepping Motor FMI-LAB Pump Model #SS50-1296
Teflon Tubing for Pump
Waters Associates Porapak R 100-120 mesh, Lot #004
Aluminum Foil
Millipore Filtration Apparatus
0.45 micron non-aqueous filter membranes
Refrigerator
Analytical Balance
Ring Stands (6)
Clamps (6)
Funnel Glass (1)

d. Chemicals:

Picric Acid "SARM", Lot #44615, PA 566
Methanol - Fisher HPLC Grade
Acetone - Fisher Certified Grade
Acetonitrile - Fisher HPLC Grade
Tetrabutylammonium hydroxide solution (25% in Methanol) "Baker" Grade for titrant use.
Phosphoric Acid - 85% Fisher HPLC Grade
Standard H_2O - 1.48 g Na_2SO_4 per 1 liter of
1.65 g NaCl distilled H_2O

4. Standards

Primary Standard Stock = 50.20 mg to 50 mL in Methanol
= 1040 mg/L

a. Working Standards:

2.5 mL of stock to 100 mL = 26.0 mg/L (I)

This dilution was made in methanol. All subsequant dilutions were made in distilled H_2O

1 mL (I) to 10 mL	=	2.6 mg/L (II)
5 mL (I) to 100 mL	=	1.3 mg/L (III)
2.5 mL (I) to 100 mL	=	.65 mg/L (IV)
1 mL (II) to 10 mL	=	.26 mg/L (V)
1 mL (III) to 10 mL	=	.13 mg/L (VI)
1 mL (IV) to 10 mL	=	.065 mg/L (VII)
1 mL (V) to 10 mL	=	.026 mg/L (VIII)

b. Control Spikes:

All dilutions were made in H_2O

1 mL of stock to 1000 mL = 1.04 mg/L (I)

10 DL	=	50 mL (I) to 1000 mL	=	52.0 µg/L
5 DL	=	25 mL (I) to 1000 mL	=	26.0 µg/L
2 DL	=	10 mL (I) to 1000 mL	=	10.2 µg/L
1 DL	=	5 mL (I) to 1000 mL	=	5.2 µg/L
.5 DL	=	2.5 mL (I) to 1000 mL	=	2.6 µg/L

5. Procedure

a. Preparation of Sorbent Tubes:

The packed sorbent tube is pretreated by pumping 50 mL of .05M tetrabutylammonium hydroxide in methanol, then 50 mL of methanol (or until HPLC analysis shows that all the impurities are removed) then 50 mL H_2O through the tube. The pretreated columns are capped to prevent moisture loss and store at room temperature until needed.

b. Sampling with Sorbent Tubes:

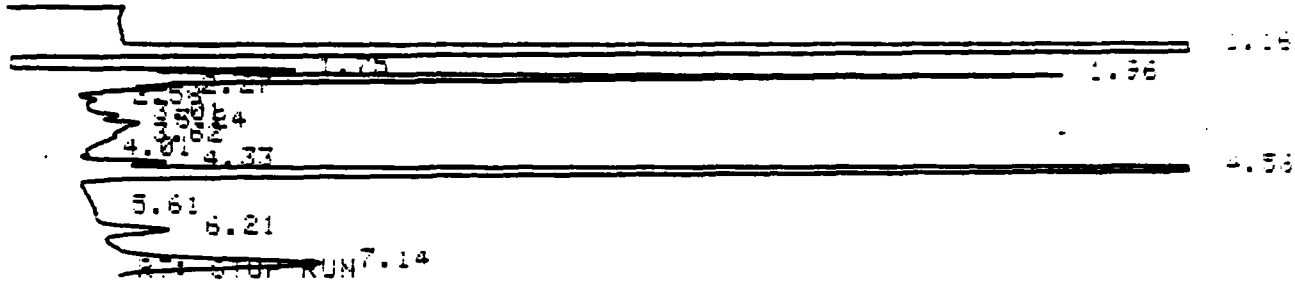
The sorbent tube is clamped in the vertical position, the end cap removed, and a piece of aluminum foil is wrapped around the tube The delivery end of the pump is connected to the sorbent tube by means of teflon tubing and a swagelok fitting. The teflon tubing from the suction end of the pump is placed in the water to be sampled. For QC, 1 liter of spiked standard water is pumped through the sorbent tube. This solution is covered with aluminum foil to prevent photodegradation of the explosive. Although the pumps are calibrated for constant delivery, it is best to accurately measure the water flowing through the sorbent tube by either pumping a measured volume through the tube or measuring the volume from the tube. After the sorbent tube is loaded, it is capped, wrapped tightly with aluminum foil, and stored at 4°C (for up to 4 weeks) to await analysis. The pump and tubing are rinsed by pumping 50 mL of acetone and then 50 mL of distilled water through them.

c. Desorption of Sorbent Tubes:

Previously loaded sorbent tubes are removed from the refrigerator and allowed to equilibrate to room temperature. The outside of the tip is cleaned by wiping with acetone soaked cotton. Then 2 x 3.75 mL portions of methanol - .05M in tetrabutylammonium hydroxide are completely forced through the sorbent tube with the pipet bulb resulting in 7.5 mL of collected eluate. 12.5 mL of distilled H_2O is added to each sample along with 2 drops of 1M H_3PO_4 resulting in a total of 20 mL. The samples are loaded into autosampler vials and 2 injections of 200 µL each are run. Inject standards singly before and after samples. A sample chromatograph is presented in Figure C-5.

6. Calculations

For picric acid, a line is constructed via least squares computation from the seven standards. Two runs of each sample are averaged to produce the found concentration. Peak height was used for all computations. The concentration of picric acid from the sorbent was multiplied by (20 mL extract/1000 mL H_2O) to give the found concentration in water.



PEAKS

1 - Solvent
2 - Impurity
3 - Picric Acid 4.6 min. 10 DL level
4 - Impurity

Instrumentation - Perkin-Elmer LC-601 with Perkin-Elmer #LC-55 variable UV-visible spectrometer
Hewlett-Packard 5880A GC integrator/recorder
Perkin-Elmer #LC-420 autosampler with rheodyne #7010 automated sampling valve with 200 µL sample loop

Column - Waters 10 micron ODS column 10 cm x 7 mm radial compression cartridge

Mobile Phase - 50% acetonitrile, 50% water, 0.005M tetrabutylammonium hydroxide buffered to pH 6.5 with phosphoric acid

Flow Rate - 2.0 mL/min.

UV Detector @ 205 nm

Figure C-5. Sample Chromatograpm of Picric Acid from Sorbent Tube Eluate

The raw data and calculated values are presented in Tables C-36 to C-40. The found versus target concentrations for picric acid over the four days were evaluated for their detection limit by the Hubaux and Vos (1975) formulae. In addition, the data were analyzed for standard deviation (Equation 1), percent imprecision (Equation 2) and percent inaccuracy (Equation 3):

$$\text{standard deviation} = s = \left[\frac{n\Sigma x^2 - (\Sigma x)^2}{n(n-1)}\right]^{1/2} \qquad \text{(Eq. 1)}$$

$$\text{percent imprecision} = s/\bar{x} \times 100 \qquad \text{(Eq. 2)}$$

$$\text{percent inaccuracy} = \frac{\bar{x} - \text{ppb added}}{\text{ppb added}} \times 100 \qquad \text{(Eq. 3)}$$

Table C-36. Picric Acid - Day 1

Concentration (mg/L)	Peak Height	Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
.026	19.94	0	0	50	0	0
.065	48.69	38.6	38.0	50	1.02	2.6
.130	93.52	88.1	86.9	50	2.38	5.2
.260	191.33	183.2	178.4	50	4.98	10.4
.650	469.8	520.7	517.5	50	14.36	26.0
1.30	940.3	1013.5	1023.1	50	28.2	52.0
2.60	1874.5					

Table C-37. Picric Acid - Day 2

Concentration (mg/L)	Peak Height	Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
.026	19.5	0	0	50	0	0
.065	50.4	54.36	53.17	50	1.38	2.6
.130	98.02	91.4	88.64	50	2.32	5.2
.260	191.1	295.0	279.7	50	7.45	10.4
.65	500.73	651.2	632.3	50	16.68	26.0
1.3	1010.7	1229.2	1270.2	50	32.49	52.0
2.6	1993.6					

Table C-38. Picric Acid - Day 3

Concentration (mg/L)	Peak Height	Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
.026	19.5	0	0	50	0	0
.065	50.47	40.97	38.3	50	1.01	2.6
.130	98.02	117.3	113.0	50	2.97	5.2
.260	191.1	252.05	229.4	50	6.24	10.4
.65	500.7	615.7	557.9	50	15.24	26.0
1.3	1010.7	1011.42	1207.7	50	28.85	52.0
2.6	1993.6					

Table C-39. Picric Acid - Day 4

Concentration (mg/L)	Peak Height	Injection 1	Injection 2	Concentration Factor	Found Concentration (µg/L)	Target Concentration (µg/L)
.026	19.45	0	0	50	0	0
.065	46.72	65.28	53.74	50	1.61	2.6
.130	93.64	119.25	140.77	50	3.54	5.2
.260	192.94	263.18	218.51	50	6.59	10.4
.650	475.14	575.15	549.2	50	15.40	26.0
1.3	950.3	948.38	1017.11	50	26.95	52.0
2.6	1893.8					

Table C-40 . Picric Acid Data Summary

Target Concentration (µg/)	Found Concentration (µg/L) Day 1	Day 2	Day 3	Day 4	Mean	Standard Deviation	Percent Imprecision	Percent Inaccuracy
0	0	0	0	0	0	0		
2.60	1.02	1.38	1.01	1.61	1.26	0.30	23.3	-51.7
5.20	2.38	2.32	2.97	3.54	2.80	0.57	20.4	-46.1
10.40	4.98	7.45	6.24	6.59	6.32	1.03	16.2	-39.3
26.00	14.36	16.67	15.24	15.40	15.42	0.95	6.2	-40.7
52.00	28.21	32.49	28.85	26.95	29.13	2.38	8.2	-44.0

Y = 0.5650X + 0.0942

Correlation Coefficient = 0.9946

Detection Limit = 6.98 µg/L

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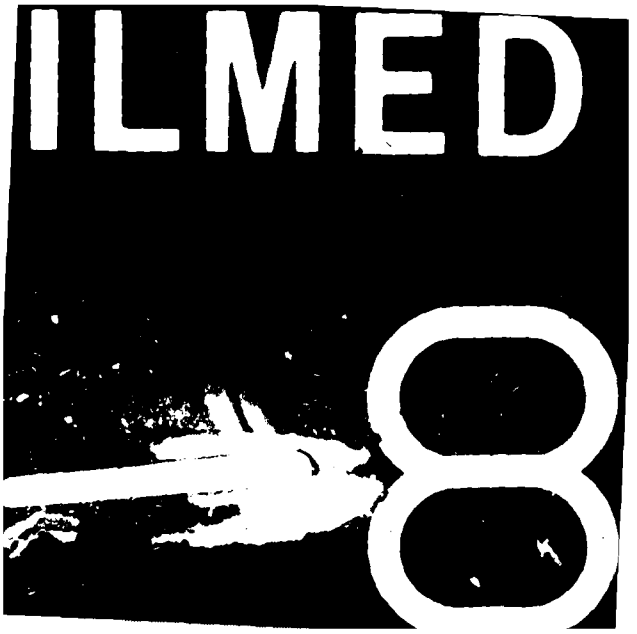
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8